Selective Hydrogenation for Industrial 1-Hexene Purification

by

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"I know the meaning of plagiarism and declare that all the work in the document, save for that which is properly acknowledged, is my own".

SYNOPSIS

Linear 1-alkenes (also frequently addressed as α-olefins) are the homologous series of compounds having one double bond at the terminal position of a linear alkane chain of four or more carbon atoms. By the end of 2005 the global demand for linear 1-alkenes (C_4- – C_{20+}) was estimated to 4.2 million tpa with the main use (more than 50%) as co-monomers for the synthesis of poly-alkenes and synthetic lubricants. Linear 1-alkenes are incorporated into polyethylene in order to impart enhanced properties to the resulting polymer such as strength and elasticity.

Most of the 1-alkenes produced worldwide are manufactured by ethylene oligomerisation while South African Sasol Chemical Industries Ltd, who are a global player in the market and were providing, for instance, more than a quarter of the world's 1-hexene in 2000, are using Fischer-Tropsch technology. Sasol are producing hydrocarbons from coal and natural gas by means of syngas conversion and extract 1-alkenes for the co-monomer market and longer linear 1-alkenes for other uses from their product mixture. Sasol isolate their 1-hexene and 1-octene by means of a sequence of complex separation processes.

In many light alkene and higher 1-alkene streams highly unsaturated trace impurities of the alkyne and alkadiene type are present. Metallocene single site catalysts utilised for ethene oligomerisation are very sensitive to such multiply unsaturated impurities. To meet the stringent conditions required to maintain high catalyst activity for the production of polyethylene, concentrations of multi-unsaturated impurities in the co-monomer stream of less than 1 ppm are required. Therefore, the removal of these trace impurities is crucial.

Selective hydrogenation processes are well established for the purification of the streams of light alkenes, such as the C_2-stream, from the steam cracker but there

are no selective hydrogenation processes available for the purification of the higher 1-alkene streams for the co-monomer market.

This work extends a series of studies performed at the Centre for Catalysis Research, University of Cape Town, on the feasibility of selective hydrogenation for the removal of highly unsaturated impurities, such as hexynes and hexadienes, that may be present in industrial 1-hexene feedstocks intended to be used as co-monomers for polyethylene synthesis. This implies that the specific aims of this study focus on the improvement and further development of the methods and techniques previously developed.

An improved experimental apparatus was designed and built that consisted of a tubular fixed bed liquid phase reactor and an upstream hydrogen dissolver to completely dissolve the co-fed hydrogen in the liquid hydrocarbon feed before reaching the catalyst bed, both mounted in a temperature controlled bath. The liquid feed mixture was pumped from the feed bottle via a metering pump. The hydrogen flow was controlled by means of thermal mass flow controllers. A sampling loop was provided downstream the reactor. Liquid product samples were collected regularly and analysed by gas chromatography using an Al_2O_3/Na_2SO_4 capillary column and a flame ionisation detector.

The choice of the catalyst, a Pd-Ag/TiO_2 eggshell catalyst (laboratory specimen provided by Süd-Chemie), the choice of the feed mixture, a solution of (as the standard mixture) 1-mol % 1-hexyne in 1-hexene, and the choice of the standard reaction conditions of 60 °C reaction temperature, 30 bar reaction pressure, a co-feed of 1 mol % hydrogen and a WHSV range from about 7 $g_{oil} / g_{cat} \cdot h$ to about 12 $g_{oil} / g_{cat} \cdot h$, were based on the experience gained from the previous studies. Impurity concentrations, the percentage of co-fed hydrogen, space velocity, reaction pressure and the amount of catalyst (by adding a second reactor or hydrogen dissolver/reactor stage) were varied. The reaction temperature (60 °C) was unchanged.

A new method was developed to more accurately determine the conversion of all of the major feed constituents, 1-hexene (98 – 99 mol % of the reactor effluent), the minor feed constituent, 1-hexyne (0.1 – 1.0 mol % of the reactor effluent) and the yield of the product, n-hexane (0.1-2 mol % of the reactor effluent) than in the previous studies. Two analyses per sample were carried out, one with a small, the other with a large volume injected, supported by high and low split ratio, respectively, in order to get accurate results from each of these analyses for the integration of the large peak and the small peaks. The two chromatograms were brought together by means of an internal standard mixture that was added to each sample prior to the two injections into the gas chromatograph.

The functionality was proofed, by a specifically designed test device and specifically developed test method, of the hydrogen dissolver applied for the purpose of getting all co-fed hydrogen completely dissolved in the liquid feed mixture before entering the reactor. The device allowed determining the 'kinetic limit' of the operational window of the dissolver. The kinetic limit determines, in addition to the thermodynamic limit that can be calculated, up to which pump rates and H_2/oil ratios complete hydrogen dissolution could actually be achieved with the given dissolver.

It could be demonstrated that the absence of gaseous hydrogen in the catalyst bed is the indispensable requirement for and the key to achieving high specificity. Specificity was defined in the previous studies as the ratio of the percentages of impurity removal to the percentage of 1-hexene loss and is, along with the degree of impurity conversion, one of the two major criteria for the evaluation of results. Indications were found, however, that limited hydrogen supply, corresponding to the stoichiometric amount required for the partial hydrogenation of the impurity to the alkene, may also be crucial once high impurity conversions are achieved.

Impurity conversion could be increased, compared to the previous studies, from about 50 % to 80 - 85 %. It was found that impurity conversion can be increased by lowering space velocity so that more of the available hydrogen can be consumed; feeding more hydrogen by increasing the H_2/Oil ratio in combination with increasing pressure (so that the hydrogen can still completely dissolve); and/or introducing a second dissolver/reactor stage for intermediate supply of additional hydrogen in order to compensate for the fraction consumed in the first reactor stage.

Specificity could be increased, compared to the previous studies, from values of about 100 to values of around 200. It was found that specificity can be increased by operating under conditions that result in very low hydrogen concentrations at the end of the catalyst bed. This can be achieved by limiting the amount of hydrogen fed so that it corresponds to the aforementioned 'stoichiometric ratio' or is only slightly higher; lowering space velocity so that most of the available hydrogen can be consumed; and/or increasing reaction pressure so that the amount of hydrogen required can be fed in one go in order to increase the initial concentration of dissolved hydrogen in the feed and thus increase the initial reaction rate and the total hydrogen consumption.

It was also found in this study that external mass transfer limitations controlled the system under the conditions applied. This problem must be tackled in future studies.

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Symbol	Description
β-PdH	Beta palladium hydride phase
FIC	Flow indicator and controller
FID	Flame ionisation detector
GC	Gas chromatograph
g_{cat}	Mass of catalyst
H_2/Oil	Molar hydrogen to total liquid feed of 1-hexene and impurity ratio
k_i	Reaction rate constant of species i
LAO	Linear alpha olefins (1-alkenes)
MTG	Methanol to Gasoline Process
MTO	Methanol to Olefins Process
PI	Pressure indicator
PIC	Pressure indicator and controller
sccm	standard cubic centimetres per minute
SHOP	Shell Higher Olefin Process
TIC	Temperature indicator and controller
Sp	Specificity
WHSV	Weight hourly space velocity
X_i	Molar conversion of species i

The acronyms specific to the internal standard method and the catalyst/process performance evaluation parameters are discussed in sections 4.5.3 and 4.5.4 respectively.

1 INTRODUCTION

Linear 1-alkenes (also frequently addressed as α-olefins) are an important group of chemicals. Linear 1-alkenes are the homologous series of compounds having one double bond at the terminal position of a linear alkane chain of four or more carbon atoms.

By the end of 2005 the global demand for linear 1-alkenes (C_4-C_{20+}) was estimated to 4.2 million tpa *(Colin, 2006)*. The main uses of linear 1-alkenes are as co-monomers for poly-alkenes and synthetic lubricants. The polyalkene co-monomers accounted for more than 50 percent of the global linear 1-alkenes demand in 2000 *(Colin, 2006).* Linear 1-alkenes are incorporated into polyethylene in order to impart enhanced properties to the resulting polymer such as strength and elasticity. Polyethylene is used in the manufacture of a wide variety of plastic products such as piping, bottles, and food and beverage containers *(Chevron Phillips Chemical, 2006).*

Linear 1-alkene producers fall into two categories: full range and on-purpose producers *(Chemsystems, 2004)*. The "full range producers" use ethene oligomerisation to produce a range of linear 1-alkenes between C_4 and C_{20}. The major full range producers are Shell, Ineos, Idemitsu Petrochemical and Chevron Phillips. The so-called "on-purpose producers" produce only selected linear 1-alkenes be it via ethene oligomerisation or be it via other routes. The demand for short (C_6-C_{10}) linear 1-alkenes for use as co-monomers is higher than that of longer ones and as such processes are being designed or optimized to produce rather narrow carbon number distributions or to rather build on-purpose plants for the production of linear 1-alkenes of a specific chain length *(Chemsystems, 2004)*.

Sasol is classified as an on-purpose linear 1-alkene producer *(Chemsystems, 2004)*. Sasol uses Fischer-Tropsch technology to produce hydrocarbons from coal and natural gas by means of syngas. Though a wide range of linear 1-alkenes is produced, Sasol only removes selected linear 1-alkenes for use as chemical feedstocks. Sasol extracts 1-hexene and 1-octene for the co-monomer market as well as longer linear 1-alkenes for use as detergent alcohols. Sasol purifies their 1-hexene by means of a sequence of complex separation processes *(Sasol, 2008)*.

It should be noted that Sasol entered the 1-alkene market only in 1994 *(Collings, 2002)* but is now a global player, producing e.g. more than a quarter of the world's 1-hexene in 2000 *(Collings, 2002)*.

Several of the new generation catalysts and processes being utilised for the manufacture of polyethylene require high purity feeds, boosting demand for high purity linear 1-alkene co-monomer feedstocks.

Lighter alkene streams are currently being purified with respect to highly unsaturated impurities such as alkadienes, ethyne and propyne, by means of selective hydrogenation. The removal of ethyne from C_2-streams from a steam cracker is undertaken using selective hydrogenation. A supported Pd-Ag catalyst is utilised with conditions varying between 10 – 36 bar and 20 – 150 °C, which is able to decrease the ethyne concentration from 2 vol % to 1 ppm vol *(Süd-Chemie, 2000)*.

This project aimed to introduce a new method of selective catalytic hydrogenation to purify industrial 1-hexene streams. If successful, this process may be utilised either as a front-end or a back-end application.

The term "selective" hydrogenation for the purification of 1-hexene streams means to hydrogenate the highly unsaturated impurities to preferentially more

1-hexene but at least with minimum hydrogenation of the 1-hexene itself to the corresponding alkane, or isomerisation to an internal or branched alkene. The aim of this project was to assess the viability of selective hydrogenation for the purification of 1-hexene, i.e. whether high impurity removal from 1-hexene can be obtained with an acceptable loss of 1-hexene.

McPherson (2003) performed liquid phase hydrogenation of 1-hexene/impurity model mixtures using a trickle bed arrangement. These studies investigated the performance of different catalysts for selective hydrogenation, with a focus on the viability of silver promoted palladium and gold as the active metals. The results were evaluated by means of activity, selectivity and specificity. Activity was defined in terms of the hydrogenation activity toward both impurity and 1-hexene hydrogenation. Selectivity was a measure of the degree of hydrogenation of both 1-hexene and impurities compared to the degree of isomerisation of both 1-hexene and impurities occurring, since minimising isomerisation is a major challenge in selective hydrogenation. Specificity, which was defined as the ratio of the conversion of impurity to the conversion of 1-hexene, has been utilised as a measure of catalyst performance. It was shown that a supported bimetallic Pd-Ag/Al_2O_3 catalyst yielded high hydrogenation activity and high selectivity. However, catalyst specificity was insufficiently low, only allowing removal of impurities together with a high loss of 1-hexene. Indications towards hydrogen mass transfer control were observed at high temperatures and low linear velocities.

Brown (2005) worked at lower hydrogen concentrations than *McPherson (2003)*, conditions that were similar to the concentrations of impurities and not exceeding the absorption capacity of the liquid feed for hydrogen. *Brown (2005)* added a hydrogen dissolution vessel prior to the reactor. By this means, *Brown (2005)* was able to avoid the presence of gaseous hydrogen in the reactor, in contrast to the previous study by *McPherson (2003)*, who utilised a high excess of hydrogen with respect to both the absorption capacity of the liquid feed and the

concentration of impurities. Under Brown's conditions, a hundred-fold increase in specificity was obtained over the same Pd-Ag/Al_2O_3 catalyst. The use of selective co-adsorbents, CO and ethanol, was also studied in an attempt to further increase the specificity but no effect was observed.

This study aimed to determine the reason for the huge increase in specificity obtained by *Brown (2005)* and to distinguish whether it was the absence of gas phase hydrogen or the low, almost stoichiometric, concentration of hydrogen. The study also aimed to increase the degree of conversion of the impurity by addition of a second hydrogen feed stream, dissolver and reactor stage.

2 INDUSTRIAL BACKGROUND

This chapter deals with the industrial background forming the basis for this project. A discussion of linear 1-alkene production is given. The need for high purity feed streams in olefin polymerisation is discussed. The likely impurities in such streams and their possible impact on downstream processing is also discussed. A review of the current understanding of selective hydrogenation for the purification of linear 1-alkene streams is presented. Research papers are discussed that deal with the influence of several process parameters (such as the choice of catalyst, in particular palladium catalysts, the addition of promoters and additives, and the reaction mechanisms) on selectivity and specificity in the selective hydrogenation of linear 1-alkenes.

2.1 The industrial importance of linear 1-alkenes

2.1.1 Linear 1-alkene producers

The main producers of linear 1-alkenes are Shell Chemicals, Ineos, Idemitsu Petrochemical, Chevron Phillips Chemical and Sasol. All these producers manufacture a range of linear 1-alkenes via ethene oligomerisation, except for Sasol who extract linear 1-alkenes of specific chain lengths from Fischer-Tropsch products made from coal derived synthesis gas, at the Sasol Synfuels complex in Secunda *(Sasol, 2008)*.

Shell chemicals market their linear alpha and internal alkene range under the trade name NEODENE (such as NEODENE* 6-XHP which is high purity 1-hexene) produced via ethene oligomerisation via the Shell Higher Olefin Process (SHOP). Shell Chemicals operates two chemical complexes which produce 1-alkenes in Louisiana in the United States and Stanlow in the United Kingdom. The Louisiana chemicals complex went into production in 1967, and

presently produces, amongst others, 1-alkenes, detergent alcohols, and ethene oxide. The plant has a capacity of 920 000 tpa of 1-alkenes. The Stanlow chemicals complex began production of 1-alkenes via the SHOP process in 1982 and currently the process has a production capacity of 330 000 tpa *(Shell, 2007)*.

BP separated its alkenes and derivatives business from its petrochemicals portfolio and in October 2005 announced its sale to UK-based Ineos. Ineos currently operates two linear 1-alkene plants in Feluy, Belgium with a production capacity of 300 000 tpa and a new facility in Alberta, Canada which started up in 2005 with a production capacity of 250 000 tpa. In 2005, Ineos (then BP) closed a linear 1-alkene production facility of 500 000 tpa in Texas in the United States *(Innovene, 2005)*.

Chevron Phillips Chemical operates two alkenes complexes. The Cedar Bayou chemical complex in Texas produces ethene, propene, linear 1-alkenes, poly 1-alkenes (for use as synthetic lubricants) and polymers such as HDPE (high density polyethylene) and LLPPE (linear low density polyethylene) *(CPChem, 2007)*. The other complex is the Q-Chem complex in Mesaieed in Qatar, producing 1-hexene *(Colin, 2006)*. The joint venture between Qatar Petroleum and Chevron Phillips Chemical went into production in 2003 with a capacity of 47 000 tpa *(Qchem, 2005)*.

Another new linear 1-alkene producer is SABIC in Saudi Arabia which produces a full range of linear 1-alkenes *(Colin, 2006)*.

Sasol selectively extracts linear 1-alkenes of specific chain lengths from the Fischer-Tropsch product for the polymers and surfactants markets. Sasol extracts 1-hexene in three 1-hexene production trains in its Sasol Synfuels complex in Secunda with total production of 200 000 tpa thereby producing a third of the world's 1-hexene. Sasol is the world's largest single-point producer *(Business Report, 2006)*.

Sasol also produces 100 000 tpa of 1-octene at the Sasol Synfuels complex in Secunda by extraction from its Fischer-Tropsch product stream. A third 1-octene train with capacity to produce another 100 000 tonnes of 1-octene per year and scheduled to go into production in mid-2008 will double Sasol's 1-octene capacity to 200 000 tpa *(Chemsystems, 2008).* The third 1-octene train is completely different to the previous trains, which merely selectively extract 1-octene from the naphtha cut from the Synthol reactors. In the new process, 1-heptene is removed from the Fischer-Tropsch product and it is hydroformylated with syngas to eventually yield 1-octene.

Sasol extracts heavier linear 1-alkenes for detergent alcohols production in the Safol™ process *(Colin, 2006).* This process may be run in a light (C_{12}/C_{13}) or heavy mode (C_{14}/C_{15}).

One of the major difficulties experienced by linear 1-alkene producers, in particular full range producers, is to balance their supply of individual linear 1-alkenes with the market requirements. This is difficult due to the wide carbon number distribution of products produced by the ethene oligomerisation process, with each product destined for different end uses whose markets are varied and dynamic.

The growth rate of the linear 1-alkene industry is 6 % per annum. There is a higher demand for linear 1-alkenes for use as co-monomers (average growth rate of 8.6 %/year expected through 2010) *(Colin, 2006)* so producers are optimising their processes to enhance the throughput of these linear 1-alkenes.

2.1.2 Processes for linear 1-alkene production

2.1.2.1 Ethene oligomerisation

Industrially, the major process route utilised for the production of linear 1-alkenes is ethene oligomerisation. Due to the ethene feedstock, only even numbered alkenes are produced. The processes are liquid phase processes making use of homogeneous catalysts.

2.1.2.1.1 Schulz-Flory type oligomer carbon number distribution

One-step processes occurring via high temperature simultaneous chain growth and desorption in a continuous mode lead to a Schulz-Flory carbon number distribution with the maximum carbon number selectivity, naturally, at C_4 *(Vogt, 2002)*. The following processes are employed for ethene oligomerisation.

The Chevron Gulf Process makes use of a Ziegler catalyst, triethylaluminium. Oligomerisation and desorption occur at 180-220 °C, 140 bar at 5 minutes residence time. The product stream has a Schulz-Flory carbon number distribution and is in the range of C_4 to C_{30}+ fractions *(Chemsystems, 2004).*

The Idemitsu Process is similar to the Gulf process but makes use of a modified Ziegler catalyst, which is more active and so may be used under milder conditions *(Kirk-Othmer, 1984).*

AlphaSelect (IFP) targets the maximizing of linear 1-alkene production in the C_4-C_{10} range using zirconium-based catalysts *(SRI Consulting, 2005).*

The Shell Higher Olefin Process (SHOP) is a three stage process of which the first step is the ethene oligomerisation stage using a homogeneous nickel catalyst. The stage is run at 120 °C, 140 bar and produces a broad carbon number distribution, consisting of linear 1-alkenes. A part of the linear 1-alkenes

is extracted, the rest of the product is sent to downstream for double bond isomerisation and metathesis steps.

2.1.2.1.2 Narrowed, Poisson type carbon number distribution

These are two step processes that make use of stoichiometric quantities of catalyst and produce a narrow carbon number distribution with maximum selectivity at a carbon number higher than C_4. The first step is batchwise oligomerisation at low temperature, until all ethene is oligomerised. The oligomers are still adsorbed onto the catalyst. In this way, the ethene/catalyst ratio, the 'stoichiometry', determines the average carbon number of the product. This is followed by displacement of the oligomers at elevated temperature. A rather narrow Poisson distribution i.e. non-Schulz-Flory carbon number distribution results *(Vogt, 2002).*

Alfen synthesis makes use of a Ziegler catalyst, triethyl aluminium, at 120 – 150 °C, 140 – 210 bar with oligomerisation time of approximately one hour. Displacement is carried out at 280 – 320 °C, 10 bar, for a few minutes.

Ineos (formally BP) also employs a Ziegler-type catalyst, triethylaluminum. The process is run so that the peak in the carbon number distribution is in the co-monomer range *(Chemsystems, 2004).*

Linear-1 technology (UOP/Union Carbide) uses a homogeneous nickel catalyst and produces C_4-C_{10} linear 1-alkenes and detergent-grade linear 1-alkenes *(SRI Consulting, 2005).*

2.1.2.1.3 Carbon number selective ethene oligomerisation

2.1.2.1.3.1 Ethene dimerisation

The Alphabutol Process (IFP) is an ethene dimerisation process, using a Ti complex with triethylaluminium. It is run at 50-55 ºC, 27-28 bar with several hours residence time *(Kirk-Othmer, 1984)*. The product is 1-butene.

2.1.2.1.3.2 Ethene trimerisation

To date, the only commercialised application of ethene trimerisation is the Q-Chem plant in Qatar. The joint venture between Qatar Petroleum and Chevron Phillips Chemical Company produces 1-hexene with 93 % selectivity *(Qchem, 2005).* The main side products are a mixture of linear and branched decenes. The process makes use of a homogeneous Cr based catalyst with a 2,5-dimethylpyrrole (DMP) ligand. The reaction is run at 115 °C and 100 bar *(Dixon et al., 2004)*.

Researchers at Sasol Technology have also reported a route to 1-hexene via ethene oligomerisation. The process, not yet commercialised, makes use of a four-component homogeneous catalyst system comprising a substituted cyclopentadiene ligand, a chromium compound, an alkyl aluminium and a halogen source *(Mahomed et al., 2003)*. The researchers report a 1-hexene selectivity exceeding 70%, with approximately 15 mass % of internal hexenes produced and higher alkenes produced in smaller quantities. The reaction is carried out batch-wise in cyclohexane at 120 °C and 50 bar.

Research is ongoing with investigations being undertaken into the use of alternative ligands *(Overett et al., 2008)* and the isolation and structural elucidation of the active catalytic species.

Kinetic and molecular modelling studies are also being undertaken to establish the actual mechanism involved in the production of internal hexenes and to deduce any structural and electronic parameters of the ligands that dictate the 1-hexene selectivity of the catalyst.

2.1.2.1.3.3 Ethene tetramerisation

Researchers at Sasol Technology have reported an unprecedented route for 1-octene via ethene oligomerisation. The novel process, not yet commercialised, makes use of a Cr based catalyst utilising a bidentate phosphine ligand and an aluminoxane activator. The researchers report a 1-octene selectivity exceeding 70%. The reaction is carried out at 35-45 °C and 30 to 45 bar.

The success of this reaction has been accredited to the mechanism of insertion of ethene into a seven-membered metallacycle that forms and subsequent elimination of 1-octene from the structure *(Walsh et al., 2006)*. Optimisation of the reactor design and reaction conditions for the catalyst system is still required before pilot studies and ultimately commercialisation can take place.

2.1.2.2 Production of 1-octene from 1,3-butadiene

The OXENO Alkenechemie GmbH company has developed a process for the production for 1-octene via reaction of 1,3-butadiene with a telomerisation catalyst and a reducing agent, to produce 1,7-octadiene and hydrogenation of the 1,7-octadiene to 1-octene.

The patent for this process states that the telomerisation catalyst is a nickel, rhodium, palladium or platinum compound or a combination of these metal compounds with a phosphine based ligand. The reducing agent is formic acid, a formate, hydrogen or a combination thereof. This process is sensitive to the presence of 1,2-butadiene which may be removed via selective hydrogenation to the alkene .

The telomerisation reaction is carried out from 40-110 °C with a hydrogen partial pressure between 1 and 64 bar. The hydrogenation reaction is carried out from 20-200 °C with a hydrogen partial pressure between 1 and 64 bar *(Beller et al., 2006).*

2.1.2.3 Hydroformylation of lower 1-alkenes

Processes using linear 1-alkenes, e.g. as co-monomers, are designed for using the even numbered ones which, originally, were all produced via ethene oligomerisation. Therefore, there is no market for odd-numbered linear 1-alkenes.

Sasol has developed a process where 1-heptene is hydroformylated with a rhodium based catalyst to produce 1-octanal, which is further hydrogenated to 1-octanol. The alcohol is dehydrated to the raw 1-octene which is purified to the final 1-octene product *(Chemsystems, 2008)*.

2.1.2.4 Thermal cracking of wax

Thermal cracking of wax produces alkenes, with up to 90 wt % linear 1-alkenes in the alkenes fraction. The process is run at 540-560 ºC, low pressures, with short contact times. However for economic reasons these processes have been abandoned *(Kirk-Othmer, 1984).*

2.1.2.5 Other processes

In addition to the above processes, especially designed for the production of linear 1-alkenes, several other processes produce alkenes as part of the product mixture, or may be run to produce alkenes. Linear 1-alkenes are a fraction of the total product from these processes.

Steam cracking of hydrocarbon fractions varying from ethane to gas oil is a pyrolysis process that is run at between 800-900 °C and low pressures. It produces low alkenes and alkanes, aromatics, alkadienes, methane and a small amount of ethyne. The process produces ethene and propene with high selectivity but shows a low selectivity of heavier alkenes. Typically, only 2 wt % of the total product is 1-butene *(Kirk-Othmer, 1984).*

Fluidised Catalytic Cracking (FCC) is a widely used refinery process, which is primarily intended for gasoline production. The process makes use of acid zeolite catalysts (essentially USHY). The reactor operates at ca. 500 °C and low pressure but may be run at more severe conditions in a light alkene mode, to increase the yield of alkenes. The linear 1-alkene yield is small due to the acid catalyst with most of the alkenes produced being highly branched internal alkenes *(Kirk-Othmer, 1984)*.

The MTG (Methanol to Gasoline) process converts methanol to alkanes and aromatics, via intermediate light alkenes. The process runs at around 400 °C, and low pressures with an acid zeolite catalyst (HZSM-5). It can be modified to run at around 500 °C to produce essentially the intermediates, namely, the light alkenes (e.g. the UOP/HYDRO MTO Process) with an alkene yield of 90%. However the product consists mostly of ethene and propene and, due to the acid catalyst, the heavier alkenes forming are essentially internal and branched *(UOP, 2007)*.

2.1.3 The uses of linear 1-alkenes

Linear 1-alkenes have a variety of uses.

- 1-Butene can be polymerised to 1-polybutene, a homo-polymer that has excellent mechanical properties such as high tensile strength and good tear properties *(Chevron Phillips Chemical, 2006)*.

- 1-Hexene is used in conjunction with 1-octene to impart special characteristics to polyethylene foils such as thinness, strength, puncture resistance and elasticity, for use as, for instance, automotive interiors, raincoats, garbage bags, cling-wrap film and other consumer plastics *(Chevron Phillips Chemical, 2006)*. It is significant to note in this context that the use of linear 1-alkenes as polyalkene co-monomers accounted for more than 50 % of the global linear 1-alkenes demand in 2000 *(Colin, 2006)*.

- C_6, C_8 and C_{10} linear 1-alkenes are also co-polymerised with vinyl acetate and vinyl chloride *(Chevron Phillips Chemical, 2006)*.

- High-performance poly linear 1-alkene based synthetic lubricants can be manufactured by oligomerising C_{10} and C_{12} linear 1-alkenes *(Chevron Phillips Chemical, 2006)*.

- 1-Decene and higher C_{12}-C_{14}, linear 1-alkenes are used to manufacture surfactants. This is undertaken via alkylation of benzene and further sulfonation to linear alkyl benzene sulfonate (LAB), a surfactant for detergent use *(Shell, 2007)*.

- C_4-C_8 linear 1-alkenes are utilised for production of linear aldehydes via OXO Synthesis for later production of short-chain fatty acids by oxidation of the intermediate aldehydes or in production of plasticiser alcohols by hydrogenation of the aldehydes *(Chevron Phillips Chemical, 2006)*.

- C_{14} - C_{18} linear 1-alkenes may be isomerised to internal alkenes which are used as a synthetic fluid base for drilling applications *(Shell, 2007)*.

- C_{16} - C_{18} linear 1-alkenes may be isomerised and reacted with maleic anhydride to form alkyl succinic anhydride. This is used as a paper sizing chemical *(Chevron Phillips Chemical, 2006)*.

- C_{12}-C_{18} linear 1-alkenes are utilised to form alkyl dimethyl amines, which are further reacted to amine oxides via oxidation with hydrogen peroxide. These are used as foam boosters in shampoos, bubble baths and dishwashing detergents *(Chevron Phillips Chemical, 2006)*.

- Heavier linear 1-alkenes are used as additives to enhance properties of waxes *(Chemsystems, 2004)*.

- Phenol or benzene can be alkylated with linear 1-alkenes to produce phenates or dialkyl benzenes which are used for manufacture of lubricants *(Chevron Phillips Chemical, 2006)*.

- Linear 1-alkenes may be used in the manufacture of epoxides, which are used to manufacture polyurethanes *(Chevron Phillips Chemical, 2006)*.

2.2 Trace impurities present in the 1-hexene product stream

As mentioned above, 1-hexene is utilised as a co-polymer in the production of polyethylene. In many 1-hexene streams, trace impurities are present. While some kinds of alkene polymerisation catalysts are unaffected by certain impurities, metallocene single site catalysts utilised for ethene oligomerisation are very sensitive to multiple unsaturated impurities *(Molnar et al., 2001)*.

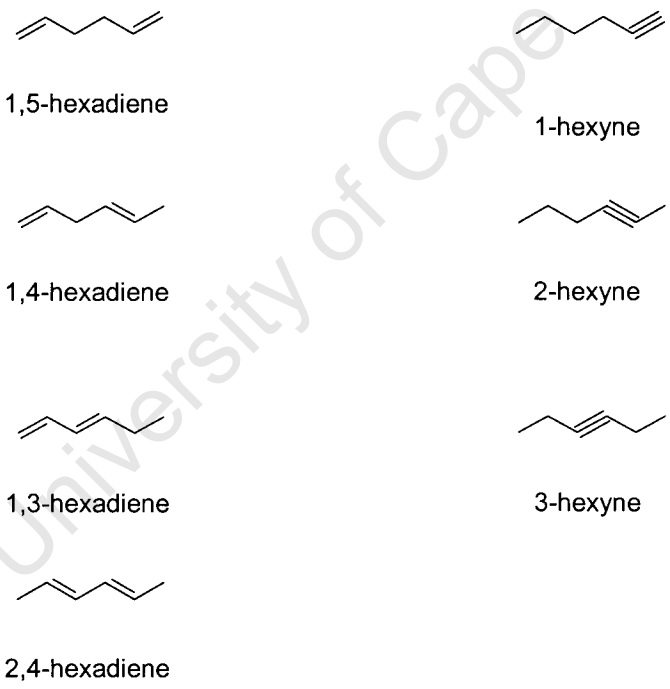

Figure 2.1 Highly unsaturated trace impurities that are likely to be present in 1-hexene streams

To meet the stringent conditions required to maintain high catalyst activity for the production of polyethylene, concentrations of multi-unsaturated impurities of less than 1 ppm are required *(Molnar et al., 2001).* Therefore, removal of these trace impurities is vital.

Although not explicitly known the respective highly unsaturated impurities are likely to comprise linear alkadienes and alkynes with terminal and internal double and triple bonds (Molnar et al. 2001). Figure 2.1 depicts the structures of these compounds.

2.3 Selective catalytic hydrogenation processes employed industrially

Selective hydrogenation over Pd/Al_2O_3 and $Pd\text{-}Ag/Al_2O_3$ has proved to be a successful process for the removal of highly unsaturated impurities from C_2-C_5 cuts from steam cracker products (section 2.1.2.6) and is widely applied.

The advantage of a catalytic process over a separation process by e.g. adsorption, is that the catalytic process not only removes the impurities but also transforms them into a valuable product which is the alkene *(Molnar et al., 2001).*

The purpose of this work is to assess the viability of this process for the removal of the aforementioned highly unsaturated trace impurities (figure 2.1) from a 1-hexene stream. This process may then be utilised as an alternative to the present purification technique employed.

The aim of selective catalytic hydrogenation of the 1-hexene stream is to hydrogenate the highly unsaturated impurities to preferentially 1-hexene, at least without hydrogenating much of the 1-hexene. If successful, this process may be utilised prior to (so-called front-end hydrogenation) or even after the current separation stages (so-called back-end hydrogenation).

In the application of selective hydrogenation on an alkene rich C_2/C_3 stream the alkynes and alkadienes in this stream are hydrogenated to the corresponding alkene(s) or alkanes. The process is able to produce e.g. a C_2 alkene product with 1 ppm ethyne that is left from an initial ethyne concentration of 0.3-2.8 vol % *(Süd-Chemie, 2000)*.

Processes are designed for front-end and back-end application of the ethyne hydrogenation reactors. In the front-end application, the steam cracker product is separated into a C_{3-} and a C_{4+} stream.

The ethyne hydrogenation reactors are placed in the C_{3-} stream and all alkyne and alkadienes in the C_{3-} stream are hydrogenated. These front-end reactors run with a large excess of hydrogen with respect to the stoichiometric amount required to hydrogenate all the impurities (10-35 mol % of hydrogen in stream).

In back-end hydrogenation, the C_{3-} stream is first separated into the different carbon number fractions and the C_2 and C_3 streams are treated individually. In this application almost stoichiometric amounts of hydrogen (with respect to the content of impurity and hydrogenation to the alkene) are added to the reactor *(Tiedtke et al., 1994)*.

The first applications of selective hydrogenation for ethyne removal were front-end applications. These reactors used Fe based catalysts and produced ethene losses. Later, back-end hydrogenation was performed instead. These processes made use of alumina supported palladium based catalysts and produced no loss of ethene.

Süd-Chemie is one of the companies that produce catalysts for selective hydrogenation applications *(Süd-Chemie, 2000)*. Chevron Phillips Chemical licensed their silver promoted palladium catalyst technology to Süd-Chemie, which is widely used in industry *(Tiedtke et al., 1994)*.

2.3.1 The C_2 cut – ethyne removal from ethene streams

Süd-Chemie's more recent research has lead to the introduction of a Pd-Ag/Al_2O_3 catalyst for the selective back-end hydrogenation of the C_2 stream. This converts ethyne to ethene and effectively adds to the ethene production. Another Pd-Ag/Al_2O_3 catalyst has been developed for the front-end selective hydrogenation of C_2/C_3 streams *(Süd-Chemie, 2000)*.

The reactions occur in the gas phase. The operating conditions for the back-end selective hydrogenation of ethyne in ethene rich streams using the Pd-Ag/Al_2O_3 catalyst are 10-36 bar, 120-150 °C, 0.9-2.2 H_2/C_2H_2 v/v *(Süd-Chemie, 2000)*.

Up to 3 ppm of carbon monoxide are added to the feed for back-end operation (though considerably more CO is required for front-end application due to the higher hydrogen content). The carbon monoxide inhibits both the hydrogenation of ethyne to ethene and the hydrogenation of ethene to ethane but it inhibits the latter reaction more and thus increases the selectivity to ethene *(Süd-Chemie, 2000)*.

Since time on stream leads to deactivation of the catalyst, two reactors are used alternatively. While one reactor is in operation mode, the other reactor is in regeneration mode (with a steam/air mixture).

The ideal molar ratio of hydrogen to ethyne is 1:1 but in practice this is usually higher because the catalyst is not totally selective towards ethyne hydrogenation to ethene.

A great advantage of the new generation Pd-Ag/Al_2O_3 catalysts is their lower tendency to form green oil. Green oil is a term describing the liquid heavy oligomers consisting of alkanes, alkenes, alkadienes and aromatics formed as a result of undesirable reactions in the process *(Kochloefl, 1995)*.

Dimerisation of ethyne produces 1,3-butadiene which is a precursor to green oil *(Süd-Chemie, 2000).* Green oil oligomers decrease the activity of both selective hydrogenation and downstream alkene polymerisation catalysts *(Molnar et al., 2001).*

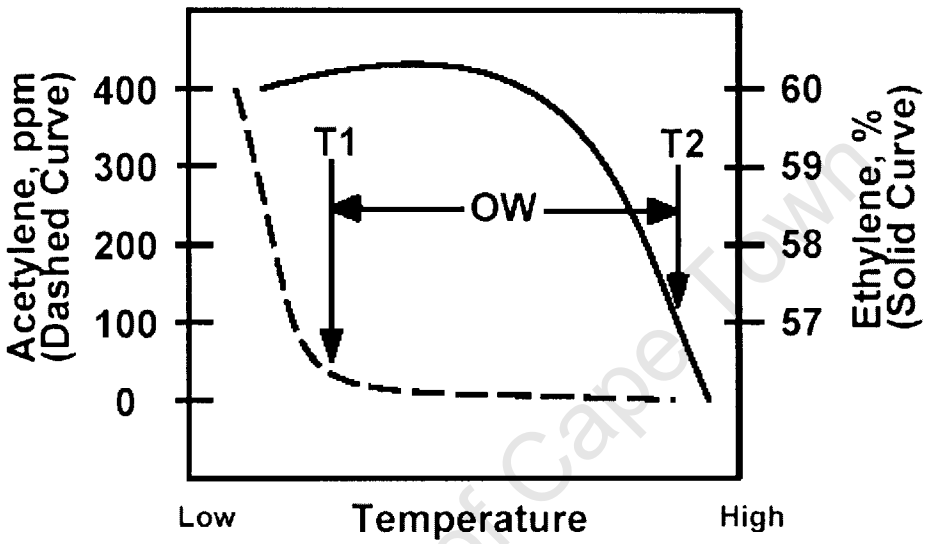

Figure 2.2 Catalyst operating window determination (Tiedtke et al., 1994)
(T1 = clean up temperature, T2 = runaway temperature, OW = operating window)

Two temperatures define the operating window for a selective hydrogenation catalyst and are a measure of the stability of the process. The temperatures are (i) that at which only a certain amount of ethyne, e.g. 20 ppm remains (referred to as the clean up temperature, T1) and (ii) the temperature at which a certain ethene loss, e.g. 3 wt % occurs (referred to as the runaway temperature, T2) (figure 2.2).

Catalysts with a large operating window allow a more thermally stable operation. A more active catalyst has a lower clean up temperature. A more selective catalyst has a wider operating window (*Tiedtke et al., 1994).*

2.3.2 The C_3 cut - propyne and propadiene removal from propene streams

Selective hydrogenation is also employed for the purification of the propene stream from the steam cracker. Here propyne and propadiene are removed in a gas phase reaction. The process is able to produce a product with only 10 ppm of these impurities from an initial concentration of 1-4 vol %. Süd-Chemie has developed a Pd-Cr/Al_2O_3 catalyst for this gas phase application. Typically, a molar H_2:propyne and propadiene ratio of 1:1 to 1.5:1 is applied.

For liquid phase application, a Pd-Ag/Al_2O_3 catalyst is employed with ten times more palladium loaded onto the support than on the gas phase operation catalyst *(Süd-Chemie, 2004)*. Liquid phase operation over the Pd-Ag/Al_2O_3 catalyst is able to increase the propene yield and to exhibit less green oil formation. As with C_2-hydrogenation, regular regeneration of the catalyst is required *(Molnar et al., 2001)*. Fouling due to oligomerisation occurs to a much lesser extent because the liquid phase removes these materials from the catalyst surface.

2.3.3 The C_4 cut - butadiene removal from the butene stream

The C_4 cut from the steam cracker contains as much as 50 wt % of 1,3-butadiene in a mixture with butenes and butane. 1,3-butadiene is a useful product and is recovered by means of extractive distillation with dimethyl-formamide (DMF) or N-methyl pyrrolidone (NMP) *(Weissermel and Arpe, 2003)*. The 1,3-butadiene (1 vol %) that is left is an impurity in the remaining C_4-alkene streams.

Selective hydrogenation in the liquid phase is employed for the removal of this 1,3-butadiene. Palladium has good activity in 1,3-butadiene hydrogenation but co-metal addition is required to increase the 1-butene selectivity *(Lee et al., 2003)*. It is possible to obtain a residual butadiene content of 10 ppm. Hydrogen mass transfer limitations are avoided by ensuring that all hydrogen is dissolved in the liquid phase *(Molnar et al., 2001)*. The additional problem of double bond isomerisation arises in the C_4 fraction that is not present in the lighter cuts. This

results in the formation of internal alkenes. In this regard, a selective co-adsorbent (CO) and the use of bimetallic catalysts improve the 1-butene selectivity.

2.3.4 The C_5 and C_6 cut - removal of gum precursors from streams to the petrol pool

2.3.4.1 Stabilisation of pyrolysis gasoline

The C_5 fraction from the steam cracker is normally sent to the petrol pool but a part of the cyclopentadiene, isoprene and isopentenes may be removed from this fraction for further processing *(Weissermel and Arpe, 2003).* Alkadienes, which are known to stabilise pyrolysis gasoline because are the precursors of gum through polymerisation in storage tanks and because these alkadienes have an unpleasant smell are selectively hydrogenated *(Molnar et al., 2001).*

Alkadienes are also highly reactive and result in the formation of oligomers which damage car engines. Supported mono-metallic palladium catalysts are utilised for the selective hydrogenation of pyrolysis gasoline *(Lin and Chou, 1994).* The selective hydrogenation of the C_5 fraction is employed in the liquid phase using a Pd/Al_2O_3 catalyst at 50-180 °C and 20-70 bar *(Molnar et al., 2001).*

2.3.4.2 Stabilisation of Fischer-Tropsch gasoline

At the Sasol Synfuels complex in Secunda, the C_5 and C_6 fractions are separated from the Fischer-Tropsch product *(Sasol, 2009).* The C_5 fraction undergoes selective hydrogenation of the alkadienes and hydro-isomerisation of the C_5 alkenes for later production of TAME (tertiary amyl methyl ether). In this process, double bond and skeletal isomerisation in the C_5 fraction is desirable because the resulting compounds have a higher octane number.

Alkene saturation is an unwanted side reaction which is limited by limiting the amount of hydrogen fed to the column. TAME is added to petrol as an octane enhancer *(Sasol, 2008)*. The C_6 fraction is sent for 1-hexene removal. The returns are processed by selective hydrogenation of alkadienes and hydro-isomerisation of the C_6 alkenes analogous to the C_5 fraction and sent to the petrol pool. In future, however, once 1-hexene has been removed from the C_6 fraction, the returns will be utilised as feed to the catalytic cracker (see section 2.3.4.3).

2.3.4.3 C_4 and C_5 catalytic cracker product processing

At the Sasol Synfuels complex in Secunda, low octane C_6-C_8 components are catalytically cracked to produce mainly low alkenes for the polymer market and high octane gasoline *(Sasol, 2008)*. In the C_4 cut of the product, the alkadienes are selectively hydrogenated to C_4 alkenes. This C_4 cut is further processed by catalytic polymerisation over solid phosphoric acid via UOP's Catalytic Condensation Process for production of petrol and diesel *(Steynberg and Dry, 2004; UOP, 2008)*. The alkadienes are coke precursors for the solid phosphoric acid catalyst which decrease catalyst lifetime. The C_{5+} cut undergoes an analogous hydrogenation process for the removal of alkadienes.

2.3.4.4 The CDHydro process

An advanced selective hydrogenation technology that is increasingly applied industrially is catalytic hydrogenation, such as the CDHydro process. CD hydro involves a catalytic distillation column along with adding hydrogen and the alkadienes are reacted over a supported palladium catalyst *(CDTech, 2008)*. A CDhydro column is typically used to selectively hydrogenate diolefins in the top section of a hydrocarbon distillation column. Additional applications – including mercaptene removal, hydroisomerisation and hydrogenation of olefins are also available (Bloch, 2006).

2.4 Thermodynamics of selective hydrogenation

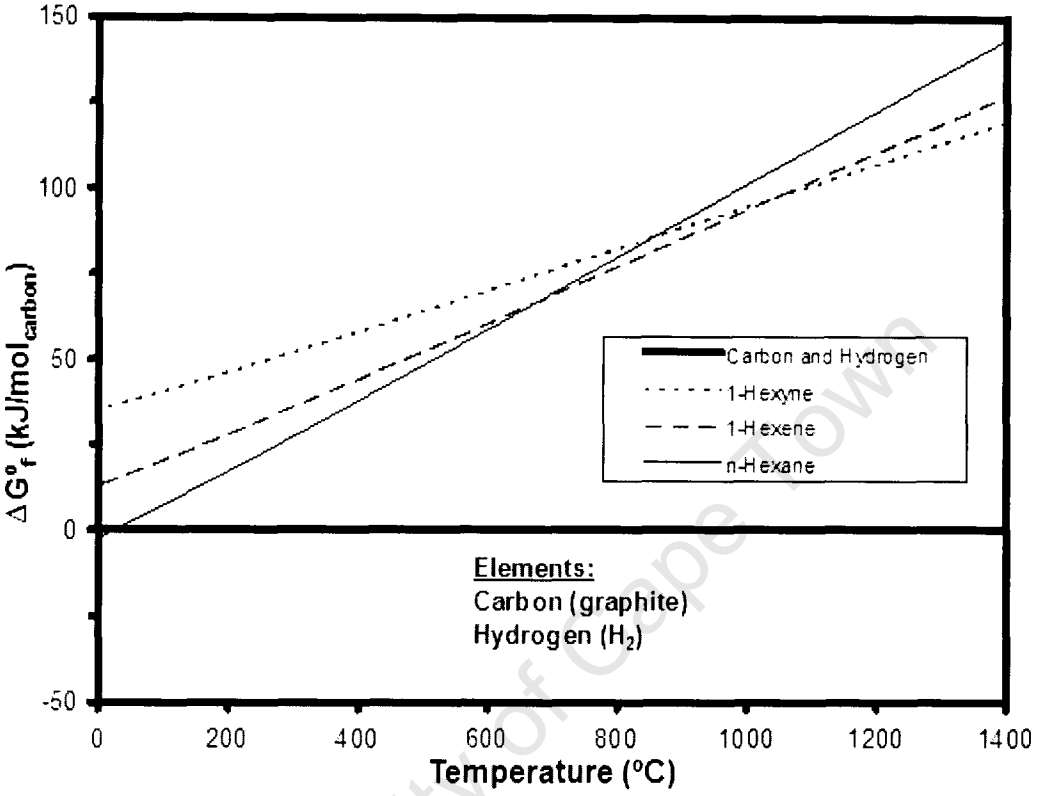

Figure 2.3 Thermodynamic stability diagram for 1-hexyne, 1-hexene and n-hexane (data from Stull et al., 1969)

Hydrogenation is an exothermic reaction. Lower temperatures favour exothermic reactions and therefore thermodynamic equilibrium will favour the formation of hexane. Conversely, at high temperatures the formation of unsaturated compounds is favoured. This is seen is figure 2.3, where the Gibbs free enthalpies of formation per mole carbon of n-hexane, 1-hexene and 1-hexyne are plotted against temperature. Isomerisation of a terminal double or triple bond is slightly exothermic and so higher temperatures would thermodynamically favour the terminal alkenes, however the differences are small compared to hydrogenation. As it may be derived from figure 2.3, at temperatures below 700 °C thermodynamics do allow but not favour selective hydrogenation of 1-hexyne to 1-hexene, so that reaction kinetics must produce the desired selectivity.

2.5 Kinetics

2.5.1 Reaction scheme for 1-hexyne hydrogenation

For this study, 1-hexyne was selected as the model impurity. Figure 2.4 illustrates the scheme of possible reactions of 1-hexyne during the purification of 1-hexene by selective catalytic hydrogenation. The reaction scheme consists of hydrogenation and double and triple bond isomerisation reactions. 1-Hexyne may be hydrogenated to 1-hexene, which may be further hydrogenated to n-hexane. It has also been postulated that a route exists for the direct hydrogenation of the impurity to the alkane *(Nijhuis et al., 2003a).* In addition to these reactions, triple and double bond isomerisation of the 1-hexyne and 1-hexene can occur. This leads to the formation of internal alkynes and alkenes, which may be further hydrogenated to the n-alkane. Skeletal isomerisation reactions are not included in the scheme. All the reactions that lead to the formation of 1-hexene are desired. Thus complete hydrogenation of the 1-hexyne is undesired. Double and triple bond isomerisation of 1-hexyne or 1-hexene is also undesired since this leads to no net removal of impurity or a loss of desired product, respectively. Obviously, any skeletal isomers forming would also be a loss.

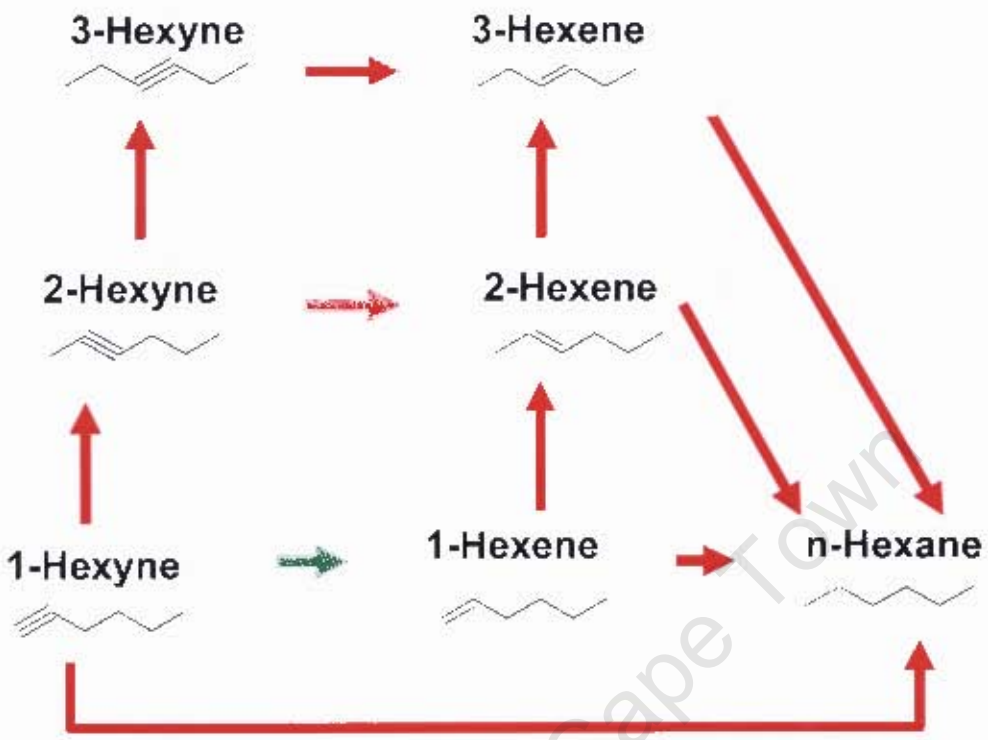

Figure 2.4 Possible reaction scheme of 1-hexyne hydrogenation

2.5.2 Reaction mechanisms

The reaction mechanisms discussed in this section are taken from *Bond and Wells (1964)*. The mechanisms presented are the basic reactions occurring on a palladium surface.

There are two generally accepted structures of the adsorbed alkene on a metal surface, the π-adsorbed alkene and the σ-diadsorbed alkene (figures 2.5 and 2.6 respectively).

The π-adsorbed alkene has the π electrons bonded to the metal surface. This π-adsorbed complex is e.g. found on palladium surfaces and only a single surface metal atom is directly involved in such an interaction (figure 2.5).

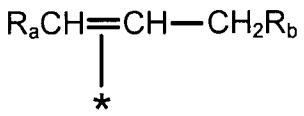

Figure 2.5 The π-adsorbed alkene (= metal atom) (Bond and Wells, 1964)*

The σ-diadsorbed alkene is formed by the rehybridisation of the carbon atoms of the double bond from sp^2 to sp^3 hybridisation followed by the formation of two σ-bonds to the surface. There are two metal atoms involved in such an interaction (figure 2.6).

Figure 2.6 The σ-diadsorbed alkene (= metal atom) (Bond and Wells, 1964)*

Hydrogenation of alkenes occurs by the addition of an adsorbed hydrogen atom to one of the bonded carbon atoms to form an adsorbed alkyl radical, which is the so-called half hydrogenated state, which is a relatively stable intermediate. The alkyl radical is further hydrogenated by a second adsorbed hydrogen atom (figure 2.7). It is uncertain whether the adsorbed alkyl radical may be formed directly from the addition of H to the π-adsorbed alkene or whether the σ-diadsorbed alkene is a necessary intermediate.

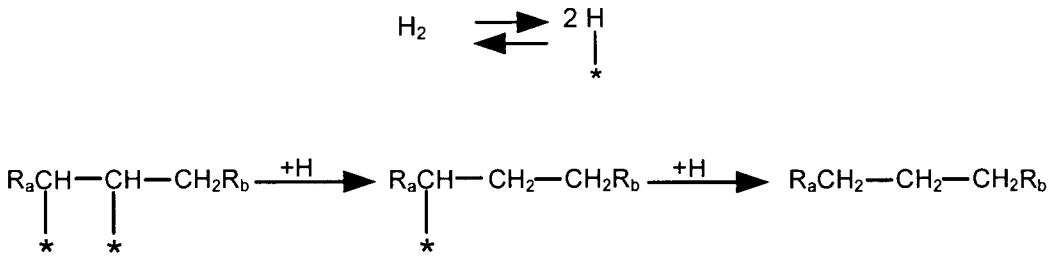

Figure 2.7 Mechanism for the hydrogenation of an alkene (= metal atom) (Bond and Wells, 1964, modified)*

For double bond isomerisation, an adsorbed hydrogen atom is added to the σ-diadsorbed alkene to form the adsorbed alkyl radical, as before. Thereafter, a hydrogen atom on the neighbouring carbon is eliminated and a new bond to the surface is formed, eventually resulting in an isomerised π-adsorbed alkene (figure 2.8).

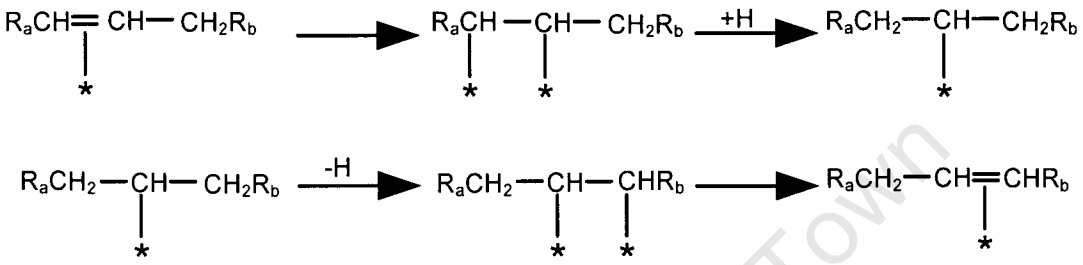

Figure 2.8 Mechanism for the isomerisation of an alkene (= metal atom) (Bond and Wells, 1964, modified)*

There are two generally accepted structures for an adsorbed alkyne *(Bond and Wells, 1964)*. In the first structure there are two sigma linkages to the metal surface retaining a double bond (figure 2.9).

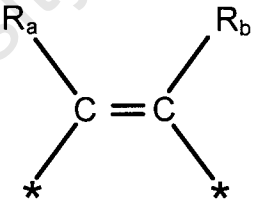

Figure 2.9 The σ-diadsorbed alkyne (= metal atom) (Bond and Wells, 1964)*

In the other structure, there are two π bonds to the metal surface (figure 2.10).

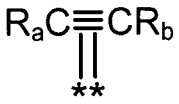

Figure 2.10 The π-diadsorbed alkyne (= metal atom) (Bond and Wells, 1964)*

In either structure the alkyne will be more strongly adsorbed onto the metal than the alkene.

The mechanism for alkyne hydrogenation is analogous to that of alkene hydrogenation (figure 2.11). The first step is the addition of an adsorbed hydrogen atom to the π-diadsorbed alkyne to form an adsorbed alkenyl radical. A second adsorbed hydrogen atom is added to yield the adsorbed alkene. The adsorbed alkene may remain on the surface and be further hydrogenated to an alkane or may desorb as an alkene.

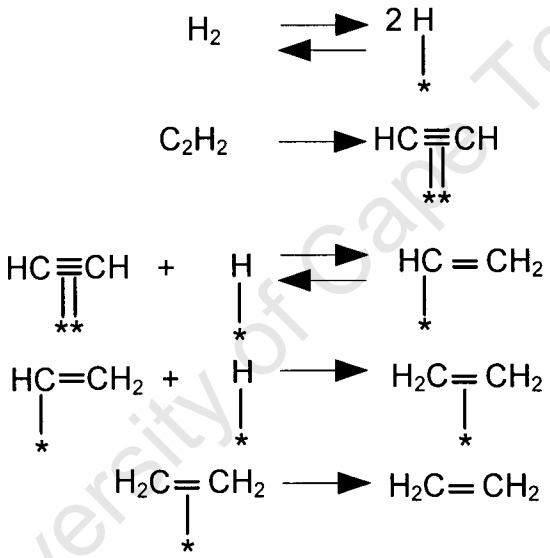

Figure 2.11 Mechanism for alkyne hydrogenation to alkene (= metal atom) (Bond and Wells, 1964, modified)*

Literature on hexyne hydrogenation mechanisms is scarce, but there is an abundance of studies on ethyne hydrogenation due to its industrial significance. The nature of the reactions at the catalyst surface is complex. There is the consecutive hydrogenation of ethyne to ethene and thereafter further hydrogenation to ethane, analogous to what is shown in figure 2.11. There is also the postulated direct route to ethane from ethyne. These results have been verified by ^{14}C labelling experiments *(Al Ammar and Web, 1978, cited in Bos and Westerterp, 1993)*. It may be possible that this "direct" route just indicates that

the alkeneic π-complex, which is the last adsorbed species in the alkyne-to-alkene reaction mechanism and equal to the first adsorbed species in the alkene-to-alkane hydrogenation mechanism, does not desorb from the surface and is further hydrogenated to ethane.

It has been proposed that multiply bonded ethylidyne and ethylidene surface species are intermediates in the direct hydrogenation to ethane *(figure 2.12, species 4 and 5) (Molnar et al., 2001).*

Several surface intermediates have been postulated to form on the working catalyst surface (figure 2.12) *(Molnar et al., 2001).*

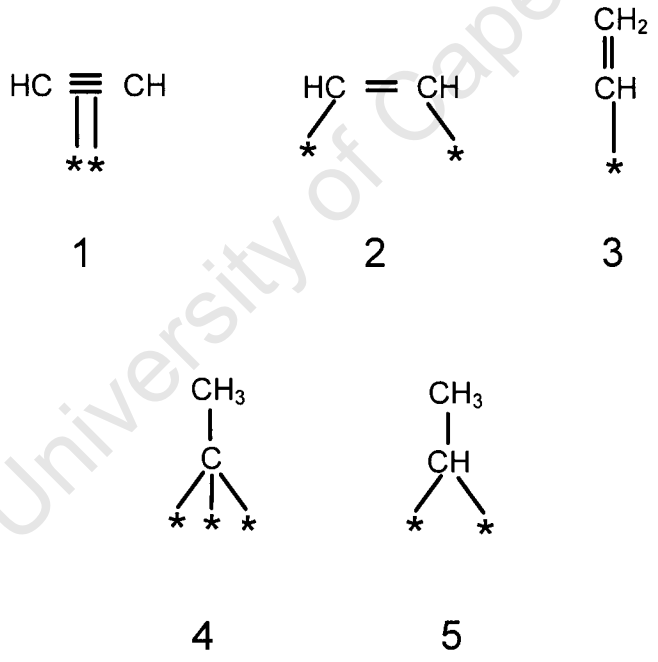

Figure 2.12 Postulated surface species involved in the hydrogenation of ethyne (= metal atom) (Molnar et al., 2001, redrawn)*

Species 1: π-diadsorbed ethyne.

Species 2: σ-diadsorbed ethyne.

Species 3: Vinyl species

Species 4: Ethylidyne species

Species 5: Ethylidene species

The species were identified using spectroscopic techniques under ultra high vacuum conditions. It is not conclusive that they are also formed under technical reaction conditions.

Species 4 to 5 have been postulated to be intermediates for the hydrogenation of ethyne to ethane.

Species 3 has been postulated as an intermediate in the route to the formation of oligomers (green oil).

2.5.3 Selectivity

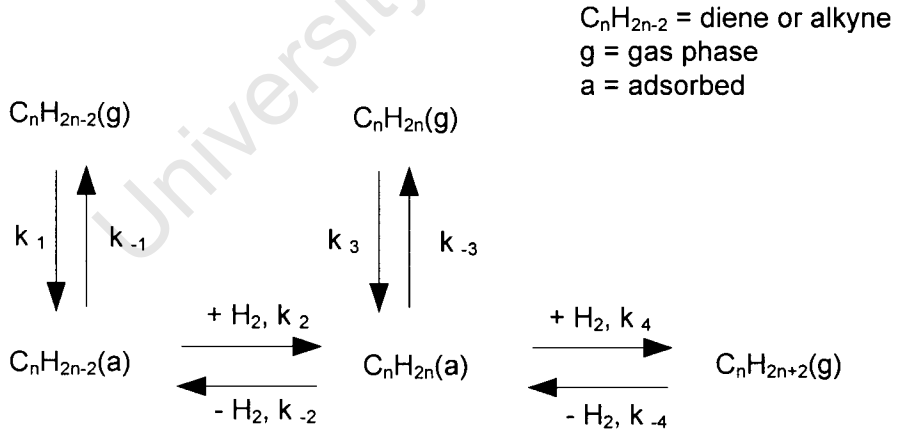

Figure 2.13 Reaction scheme of alkyne and alkadiene hydrogenation on a palladium surface (Molnar et al., 2001, redrawn)

Figure 2.13 represents the reaction scheme for the hydrogenation of a multiply unsaturated compound such as an alkyne or alkadiene impurity on a metal surface. "Mechanistic selectivity" has been suggested to occur as a result of $k_2 >> k_4$ as long as $k_{-3} >> k_4$, which results in alkene formation *(Molnar et al.,*

2001). "Thermodynamic selectivity" has been suggested to occur as a result of $k_1/k_{-1} >> k_3/k_{-3}$, that is the strong adsorption of the multiply unsaturated molecule prevents the re-adsorption of the alkene whose adsorption is weaker so that only selective hydrogenation of the alkyne is achieved. Thermodynamically, as long as there is sufficient hydrogen available, complete saturation would be favoured. Therefore, the high selectivity of alkyne hydrogenation to alkene over palladium may be attributed to the stronger adsorption of the alkyne than the alkene *(Molnar et al., 2001).*

However, mechanisms have been proposed where two types of sites are involved. *Men'shchikov et al. (1975)* studied the selective hydrogenation of ethyne in ethene over a 0.005 wt % Pd/Al_2O_3 catalyst, with mixtures of 0.0002-0.8 vol % ethyne at 20 bar and 80-160 °C, with 140 ppm CO addition. Hydrogen was added in excess of the stoichiometric amount required to hydrogenate all the ethyne to ethene. It was observed that there was no dependence of the rate of ethene hydrogenation from ethyne partial pressure. A mechanism was proposed where ethyne and ethene were adsorbed on different sites. On the one type of sites, ethyne is selectively hydrogenated to ethene. On the other type of sites, ethene is hydrogenated to ethane even in the presence of high ethyne concentrations.

2.5.4 Reaction rates

The relationship between adsorption strength and reaction rate is given in a volcano plot (figure 2.14, left). It may be seen that an optimum adsorption strength corresponds to the highest reactivity. Alkynes are adsorbed too strongly, preventing hydrogen adsorption, leading to low hydrogenation reactivity. These properties of the active metal may be changed by, for example, the addition of a second metal which leads to reduction in the adsorption strength of the alkyne so that its reactivity is increased by allowing hydrogen adsorption (figure 2.14, right) *(Coq and Figueras, 2001; Ponec and Bond, 1995).* The reactivity of the alkyne is

then higher than that of the alkene. In terms of the mechanistic selectivity, the hydrogenation of the alkene would be faster than that of the alkyne but due to the higher adsorption strength of the alkyne, the alkyne will be preferentially adsorbed and hydrogenated until the alkyne concentration is sufficiently low to allow adsorption of the alkene *(Molnar et al., 2001)*. This inter-relationship may be applied to the selective hydrogenation of ethene streams for the removal of ethyne. The ethyne adsorbs preferentially onto the palladium surface. As long as there is sufficient ethyne to cover all the palladium sties, only ethyne will be hydrogenated. As soon as ethene is formed, it desorbs from the metal surface and is replaced by another ethyne molecule. This prevents further hydrogenation to ethane *(Tiedtke et al., 1994)*. Therefore it is important to design a catalyst and operate under conditions such that the concentration of ethyne is kept high on the catalyst surface to prevent the adsorption of ethene, which may otherwise be further hydrogenated.

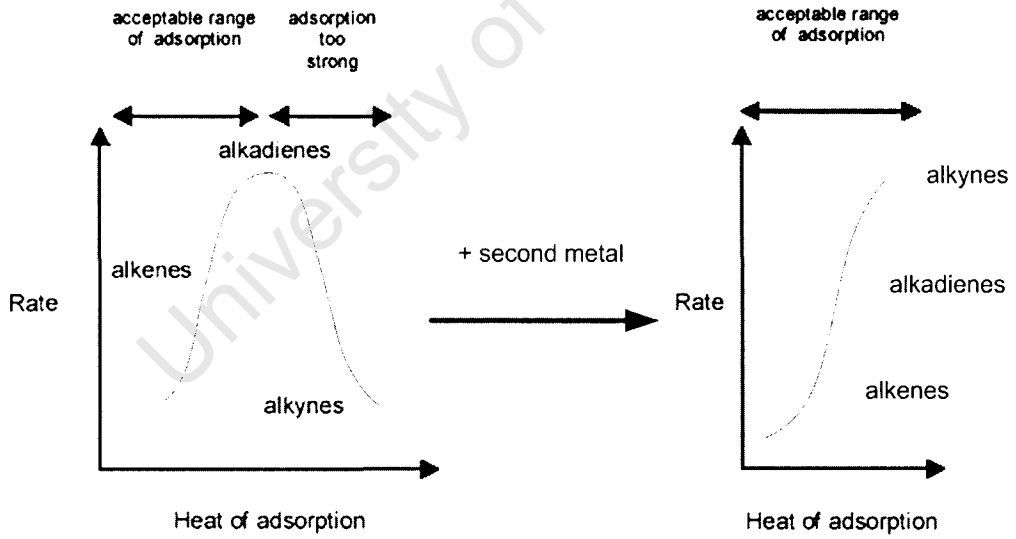

Figure 2.14 Relative rates of alkene, alkadiene and alkyne hydrogenation as a function of their heat of adsorption on palladium catalysts (left) and promoted palladium catalysts (right) (Coq and Fiqueras, 2001, redrawn)

Experiments by *Walter et al. (1993)* confirm this. A steam cracker C_4 product that contained about 40% 1,3-butadiene was selectively hydrogenated over a palladium catalyst under excess hydrogen in a stirred isothermal batch reactor (no other reaction conditions are given). With increase of residence time the 1,3-butadiene concentration declined and the n-butene concentrations increased while the n-butane concentration was constant. After the alkadiene concentration was down to 2-3 % residual 1,3-butadiene, the concentration of 1-butene passed through a maximum and then declined and the concentration of n-butane started increasing, see figure 2.15. These observations confirm the inhibiting effect of a high concentration of strongly adsorbed highly unsaturated species on alkene hydrogenation.

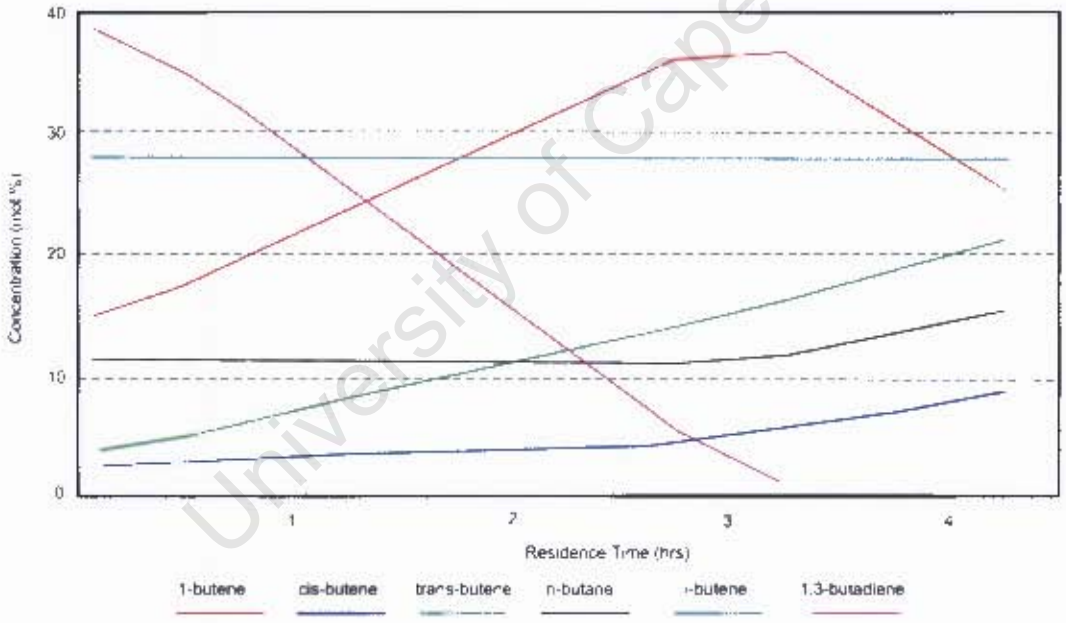

Figure 2.15 Concentration of constituents vs. residence time during the selective hydrogenation of 1,3-butadiene in a C_4 steam cracker cut (Palladium catalyst, batchwise, excess hydrogen), Walter et al. (1993)

Walter et al. (1993) point out that the position of the 1-butene maximum relative to the residual 1,3-butadiene content varies depending on the catalyst. It is also pointed out that "there are some additional factors which influence selectivity"

before discussing the effects of internal mass transfer and metal distribution (section 2.9).

2.5.4.1 Rate laws and reaction orders

Kinetic data for selective hydrogenation are very scarce in the literature and usually rate laws devised are only applicable to a very narrow range of reaction conditions.

Sales et al. (2000b) converted hexadienes (2 wt % in n-heptane) over Pd/Al_2O_3 and $Pd\text{-}Ag/Al_2O_3$ catalysts at 40 °C and 1 bar and found the reaction to be first order in hydrogen and zero order in the hexadienes.

Walter et al. (1993) obtained a linear decrease in 1,3-butadiene concentration when selectively hydrogenating a 1,3-butadiene-rich C_4 fraction from steam cracking over a palladium catalyst under excess hydrogen in a stirred isothermal batch reactor (no other reaction conditions are given), see figure 2.15. This was interpreted as an indication towards a reaction order of zero for butadiene. It was observed that this linear decrease lasted until a residual 1,3-butadiene concentration of 2-3% was reached, then levelled out. As can be seen from figure 2.15, hydrogenation of 1-butene to n-butane started at the same concentration, indicating that the catalyst surface was no longer completely covered by the 1,3-butadiene. The levelling out of the 1,3-butadiene concentration curve at the very low concentrations indicates a higher reaction order for 1,3-butadiene hydrogenation than zero.

Godinez et al. (1995) fitted a kinetic model to their data from the selective gas phase hydrogenation of the alkynes and alkadienes (0.8 mol %) in steam cracking C_2/C_3 streams. *Godinez et al. (1995)* worked at 1 bar total pressure and 60-80 °C and in presence of up to 0.2 mol % CO over two Pd/Al_2O_3 catalysts and found reaction orders of one for hydrogen and zero for the highly unsaturated

compounds. It should be noted that zero order for the highly unsaturated compounds was observed even at the very low concentrations and partial pressures applied.

McPherson (2003) also found the rate law being zero order with respect to alkadiene concentration from experiments in trickle phase reactors at 55-65 °C and 15 bar hydrogen partial pressure.

2.5.5 Simplified pseudo-parallel reaction scheme

From the reaction scheme presented (figure 2.4), it follows that a complex series of consecutive and parallel reactions may occur on the surface. Double or triple bond isomerisation is not considered a desirable reaction since it does not result in a net removal of impurities. Total hydrogenation of the impurity or hydrogenation of the bulk, the alkene species, is also not desired since the alkene is much more valuable. At present, the mechanisms occurring on the palladium surface are not clear and as such few rate expressions describing this system are available.

McPherson (2003) describes the system in terms of a simplified pseudo-parallel reaction scheme. The reaction scheme was simplified into a system of two lumped pseudo-parallel reactions as follows:

- Removal of impurities and impurity isomers by hydrogenation (desired).
- Loss of 1-alkene via hydrogenation or isomerisation (undesired).

The lumped reactions were assumed to be first order with respect to hydrocarbon concentration and have the same dependence on hydrogen partial pressure i.e. these terms will cancel off resulting in no dependence from hydrogen partial pressure.

"Specificity" was defined as a measure of the overall catalyst and process performance in terms of the ratio of conversions in desirable and undesirable reactions *(McPherson, 2003)*:

$$Sp = \frac{X_{impurity + impurity\ isomers}}{X_{1-hexene}} \qquad (2.1)$$

Where $X_{impurity + impurity\ isomers}$ refers to the removal of all of the impurity and its isomers that may possibly form.

A specificity of one indicates that the rate of the removal of impurity is equal to the rate of loss of 1-hexene (assuming first order in concentration of the respective hydrocarbon). Specificities higher than one indicate that the rate constant of the removal of impurity is higher than the rate constant of loss of 1-hexene.

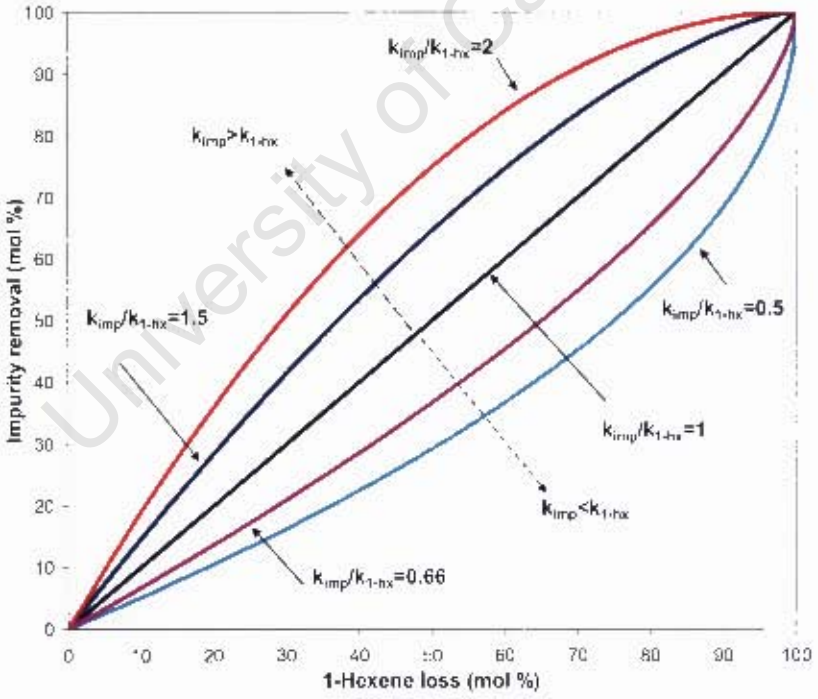

Figure 2.16 Idealised specificity plot (McPherson, 2003, redrawn) (k_{imp} and $k_{1\text{-}hx}$ = rate constants of impurity removal and 1-hexene loss)

A graph of removal of impurity vs. loss of 1-hexene was plotted *(McPherson, 2003)*. The initial slope (i.e. at low conversions) of this curve will then quantify the specificity. An idealised specificity plot is given in figure 2.16. It is desired that the loss of 1-hexene be low and the removal of impurities be high. This would correspond to a curve with a steep initial slope, i.e., a high specificity.

"Selectivities" were defined as the ratio of loss/conversion of 1-hexene or impurity via hydrogenation to loss/conversion of 1-hexene or impurity via isomerisation *(McPherson, 2003)*. It is desired to obtain a high selectivity because isomerisation does not lead to net removal of impurity. *McPherson (2003)* noted that only minor isomerisation of 1-hexene took place with the catalyst utilised in the present study (Pd-Ag/TiO_2). Selectivity was >95% at 65 °C and 15 bar hydrogen partial pressure. Selectivity increased with increasing hydrogen partial pressure.

2.6 Metals used as catalysts in selective hydrogenation applications

Palladium has long been the metal of choice for selective hydrogenation applications for removal of alkadienes and alkynes from technical alkene streams (section 2.3). Numerous studies abound in which the selectivity and activity of these catalysts for particular applications has been optimised.

The maximum catalytic activity is a result of an optimum strength of adsorption of impurities and intermediates onto the metal surface. The partially hydrogenated intermediate formed from a highly unsaturated reactant at the surface must be stable enough to be formed but not too stable to desorb from the surface *(Coq and Figueras, 2001)*. The high reactivity of palladium for hydrogenation of ethyne to ethene may be attributed to the interaction of the metal with the alkyne species which is strong enough to enable adsorption and reaction, but not too strong to prevent desorption of the partially hydrogenated product *(Molnar et al., 2001)*.

Ultra-fine gold particles dispersed on supports have recently been found to be very active for several chemical reactions. The hydrogenation of ethyne was studied using ultra-fine Au/Al_2O_3. The catalyst was shown to be very selective to ethene from 40-250 °C with ethane only being formed at higher temperatures. The high selectivity was attributed to the weak adsorption of ethene on these ultra-fine gold particles. The activity of the catalyst was shown to be dependant on the size of the ultra-fine gold particles with a maximum around 3.0 nm *(Jia et al., 2000). McPherson (2003)* investigated the use of gold on titania as a possible catalyst for selective hydrogenation of impurities in 1-hexene but observed a very poor hydrogenation activity. However, no information was given about the size of the gold particles, nor was any optimisation reported *(McPherson, 2003)*.

A Cu/SiO_2 catalyst was employed for the gas phase hydrogenation of 1-butyne and 1,3-butadiene *(Koeppel et al., 1994)*. The feed mixtures utilised were 0.5-3.0 mol % of 1,3-butadiene, and 4 mol % hydrogen in helium as well as 0.5-2.5 mol % of 1-butyne and 4 mol % hydrogen in helium. The conditions utilised were 110 °C, and atmospheric pressure. The results showed the absence of butane formation as well as negligible isomerisation proving that this catalyst is highly selective for the formation of linear 1-alkenes.

2.7 The role of promoter metals

Industrial catalysts utilised for the purification of industrial C_2-C_5 streams from the naphtha steam cracker make use of bi-metallic catalysts to affect higher selectivity to the alkenes. Numerous studies abound in the literature on the enhancement of alkene selectivity by addition of a second metal to supported palladium catalysts. A review by *Coq and Figueras (2001)* summarises the reasons for this selectivity enhancement.

Maximum catalytic activity is obtained at an optimum adsorption strength of the alkyne. Alkynes are too strongly bonded onto the surface of pure palladium,

especially on small metal particles which are electron deficient *(Molnar et al., 2001).* The addition of a second metal to the palladium in the form of an alloy changes the electronic structure of the palladium, decreasing the adsorption strength of the alkynes on the palladium surface hence increasing catalyst activity (figure 2.14). This has been defined as the "electronic effect" (section 2.9.3).

Boitiaux et al. (1993) point out that such additives must be added directly during catalyst preparation and that the additive must interact directly with the palladium through electron donation, with group IB metals being particularly good candidates.

The addition of a second metal may also result in an alloy that has a higher activity than either of the contributing metals individually; such sites have been defined as mixed sites *(Molnar et al., 2001).*

Some undesirable side reactions have been shown to require more than one surface atom to proceed. These reactions require an ensemble or the close proximity of active surface metal atoms. They are suppressed by adding a second metal. The effect of addition of a second metal is explained in a way that the active metal, e.g. palladium, is diluted by an inert metal, e.g. silver, in order to decrease the size of these ensembles. Isomerisation of alkenes requires such an ensemble of sites in order to proceed *(Sales et al., 2000b)* so the addition of the second metal results in a decrease in isomerisation and enhance the selectivity to the linear 1-alkene. This has been defined as the "geometric effect" or the "ensemble size" model.

Another specificty enhancement effect, demonstrated by the addition of a second metal, is the avoidance of a β-PdH phase which will be discussed in section 2.10. Below are listed some findings reported in literature which demonstrate the specificity enhancement obtained by addition of a second metal to a selective hydrogenation catalyst.

Furlong et al. (1994) conducted a comparative study on the effect of the addition of copper to Pd/Al_2O_3 on the selective hydrogenation of 1,3-butadiene to 1-butene in the gas phase. The study was undertaken at atmospheric pressure in a plug flow reactor at 15-40 °C with 9 mol % 1,3-butadiene in 1-butene and a H_2/1,3-butadiene molar ratio of 1.6. It was observed that the addition of copper increased specificity by decreasing complete hydrogenation and isomerisation of the alkene. Under the conditions of the study, the addition of copper resulted in an increase of the total selectivity to butenes from 50% to over 99%. It is significant to note that this means that less than 1 % of the 1-butene was hydrogenated. Hydrogen sorption experiments revealed that addition of copper resulted in a decrease in the availability of atomic hydrogen for the surface reaction. However, it was not clear whether this was due to alloy formation or copper adsorption at the active sites decreasing the palladium ensemble size, in other words whether the increase in butene selectivity by the addition of copper was due to electronic or geometric effects. Catalyst deactivation was observed for all catalysts tested which was attributed to the oligomerisation of alkenes, but this did not account for the increased selectivity.

Nijhuis et al. (2003a) also studied the effect of the addition of copper to a silica supported palladium catalyst for the liquid phase selective hydrogenation of 3-methyl-1-pentyne-3-ol dissolved in ethanol. The concentration of 3-methyl-1-pentyne-3-ol in ethanol was 0.3 mol/l. The reaction was undertaken in a batch reactor at 1.1 bar hydrogen pressure and 25 °C. The addition of copper resulted in an increase in alkene selectivity which was explained by the electronic interaction of copper with the palladium crystallites, which decreased the relative adsorption strength of the alkene. It was also postulated that copper addition decreased the size of ensembles of palladium, assuming that alkene hydrogenation required larger ensembles than alkyne hydrogenation.

The Lindlar catalyst is also utilised for the selective hydrogenation of alkynes. This catalyst consists of $CaCO_3$ supported palladium poisoned by lead diacetate.

Under reaction conditions, the lead diacetate is reduced to lead *(Molnar et al., 2001).* Several studies, as reviewed by *Molnar et al. (2001),* shed light on the role of lead in the Lindlar catalyst. These studies provide corresponding explanations as to the role of lead, with one study stating that lead does not form an alloy with palladium and, correspondingly, the other study stating that lead did not change the electronic properties of the palladium crystallites. It has been postulated that lead addition blocks sites responsible for unselective hydrogenation.

Zhang et al. (2000) studied the effect of silver addition to an alumina supported palladium catalyst for the selective hydrogenation of ethyne in ethene. The reactions were undertaken in the gas phase with a H_2/ethyne molar ratio of 52.5, and a pressure of 16 bar, from 30-52.5 °C for the monometallic catalyst and from 50-105 °C for the bimetallic catalyst. It was observed that the activity of the bimetallic catalyst was lower than that of the mono-metallic palladium catalyst. However, at 100 % ethyne conversion, the ethene selectivity of the bi-metallic catalyst was higher. Higher temperatures resulted in lower ethene selectivity for both catalysts, with the bimetallic catalyst displaying a smaller decrease in ethene selectivity with a temperature increase than the monometallic catalyst. X-ray photoelectron spectroscopy (XPS) showed the formation of a Pd-Ag alloy on the alumina surface. The authors concluded that the enhancement in selectivity by silver addition may be attributed to the decrease of the number of large ensembles of active palladium atoms. The change in the electronic structure of the palladium crystallites has been considered to have only a minor effect.

Sales et al. (2000b) investigated the selective hydrogenation of 1,5-hexadiene in the liquid phase on an alumina supported palladium catalyst with addition of silver. The reactions were undertaken at 40-50 °C, atmospheric pressure and a solution of 2 wt % 1,5-hexadiene in n-heptane. For the monometallic palladium catalyst, 1-hexene predominates the product at low conversion, while 2-hexene predominates at high conversion. Adding silver increased the selectivity to 1-hexene even at high conversions but decreased the activity. This has been

explained in terms of the geometric effect of dilution of palladium atoms, which inhibits isomerisation. Another explanation is the absence of the β−PdH phase in the bimetallic catalyst (section 2.10), which was confirmed via temperature programmed reduction.

Sarkany et al. (2002) studied the selective hydrogenation of ethyne over Pd/SiO_2 and $Pd\text{-}Au/SiO_2$ catalysts. Higher ethene selectivity over the bimetallic catalyst was observed which was attributed to the dilution of the palladium with gold atoms, which breaks up large ensembles. These large ensembles were responsible for the adsorption of multiply bonded species such as ethylidyne and ethylidene species (species 4 and 5, figure 2.12) which are postulated to be intermediates for the hydrogenation of ethyne to ethane.

Kang et al. (2000) studied the selective hydrogenation of ethyne on Pd/SiO_2, with the effect of Ti, Nb and Ce oxide addition being investigated. The study was undertaken with 0.9 mol % ethyne in ethene at 40 °C with a hydrogen/ethyne molar ratio of 2 (pressure not stated). The results showed that the addition of the transition metal oxides to the monometallic catalyst increased the catalyst activity and ethene selectivity. This was attributed to the interaction between palladium and the metal oxides which alter the geometric and electronic properties of the catalyst surface. X-ray photoelectron spectroscopy showed that the metal oxides are highly populated on the palladium surface, which block the formation of large palladium ensembles and thus block multiply-bonded intermediates being formed on the palladium surface. They suppress direct formation of ethane and formation of oligomers. The metal oxides also donate electron density to the palladium crystallites which weakens ethene adsorption. Sintering of the dispersed palladium is also suppressed which maintains catalyst activity.

Similar results have been observed for the selective hydrogenation of 1,3-butadiene on Pd/SiO_2 where the surface has been modified with addition of TiO_2 *(Lee et al., 2003).* The reaction was undertaken at 50 °C with a 2 mol % hydrogen, 0.25 mol % 1,3-butadiene, 2.25 mol % 1-butene mixture in nitrogen. It

was observed that the addition of TiO_2 increased the 1-butene selectivity. The results indicated, similarly, that partially reduced titania species decorate the palladium surface altering the electronic state of the palladium. This decreases the 1-butene adsorption strength on palladium facilitating 1-butene desorption from the surface. These titania species on the surface also block large palladium ensembles, which are responsible for multiply bonded intermediates which are isomerised or undergo full hydrogenation to the alkane.

The effect of palladium addition to an alumina supported cobalt catalyst for the selective hydrogenation of 1,3-butadiene has been investigated by *Sarkany et al. (1995).* The reactions were undertaken with a mixture of 9 mol % 1,3-butadiene in 1-butene and a H_2/1,3-butadiene molar ratio of 2. The authors postulated the presence of intermetallic phases formed between cobalt and palladium. A decrease in the Pd/Co ratio resulted in a higher selectivity to butenes but increased isomerisation to internal butenes. The accumulation of carbonaceous deposits on the catalyst was observed. It was not possible to determine equivocally whether the observed increase in selectivity was to due to electronic effects or selective poisoning of cobalt sites.

In conclusion

It was found that the addition of a second constituent to the palladium base metal of the catalysts, preferentially silver, but also other metal or metal oxides, improved the performance of selective alkyne and alkadiene hydrogenation catalysts. This improvement refers essentially to the preference of alkene over alkane formation from the highly unsaturated species while activity is less affected and often declines. The improved selectivity is attributed to both the inhibition of ensemble formation and electron donation effects.

As Boitiaux et al. (1993) point out, such additives must be added directly during catalyst preparation and that the additive must interact directly with the palladium through electron donation, with group IB metals being particularly good candidates.

2.8 Support materials used for catalysts in selective hydrogenation applications

Most catalysts utilised for the purification of industrial C_2-C_5 streams from the naphtha steam cracker make use of alumina as a support material *(Süd-Chemie, 2004).* Other than alumina, the most commonly used supports are silica, titania and carbon.

Alumina is weakly acidic and has been shown to effect a significant extent of double-bond isomerisation in purification of commercial C_8 linear 1-alkene streams which results in an excessive loss of linear 1-alkene feedstock under typical selective hydrogenation conditions *(McPherson and Fletcher, 2000).* In a further study, *McPherson (2003)* studied selective hydrogenation of highly unsaturated hydrocarbons in 1-hexene, using Au/TiO_2, $Pd\text{-}Ag/TiO_2$ and $Pd\text{-}Au/SiO_2$. *McPherson (2003)* described how hydrogenation and isomerisation functions are attributed to different centres on the catalyst. The metal is responsible for the hydrogenation whilst the isomerisation is facilitated by acid sites on the support. Therefore, to increase the selectivity of the catalyst, which means to promote reaction via hydrogenation rather than isomerisation, the acid function of the catalyst must be suppressed. This was undertaken by the use of a non-acidic support. The results of *McPherson (2003)* confirmed that the use of titania support led to lower extents of isomerisation than the alumina support.

A study by *Brayner et al. (2000)* investigated the use of palladium supported on niobia as a catalyst for the selective hydrogenation of 1,5-hexadiene and compared these results to a Pd/Al_2O_3 catalyst. The reaction was undertaken in the liquid phase, batch-wise, with a 2 wt % 1,5-hexadiene in heptane solution at 40 °C. The niobia supported catalysts were prepared by several techniques which produced mainly low dispersion catalysts. In spite of this, the selectivity to

1-hexene, as well as the total selectivity to hexenes was higher than over the alumina supported catalyst.

The use of palladium catalysts supported on heterocyclic polyamides was investigated by *Michalska et al. (1998)*. In this study, palladium was inserted into the heterocyclic polyamide via ligand exchange and utilised for hydrogenation of alkadienes and alkynes. Amongst the compounds tested, were 2-hexyne, 1-octyne and 1,7-octadiene. The reactions were undertaken in the liquid phase, batch-wise, at 25 °C and 1 atm with 10 vol % of substrate in a solvent. In the selective hydrogenation of 1,7-octadiene, 70% selectivity to 1-octene was obtained, whilst in the selective hydrogenation of 2-hexyne a selectivity of 81 % to hexenes was obtained. The high selectivity of the catalyst was explained by the electron donating properties of the support which altered the co-ordination of the palladium which favoured desorption of the alkenes.

2.9 The role of catalyst particle size, metal distribution and dispersion

The catalysts utilised for the hydro-purification of industrial C_2-C_5 streams from the naphtha steam cracker are high metal dispersion egg shell type catalysts *(Süd-Chemie, 2004)*.

2.9.1 Catalyst particle size

It is known that the selectivity to the intermediate B in a reaction sequence $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ depends on the Thiele Modulus, that is, for instance, the particle size. In the case of $k_2 > k_1$, even a Thiele Modulus < 1 has a detrimental effect on intermediate selectivity as determined by *Wheeler (1951)* and *Wei (1962a, 1962b)* and demonstrated experimentally, for instance, by *Moller et al. (1998, 1999)*.

The effect of catalyst particle size on the conversion of highly unsaturated impurities in a model C_2/C_3 alkene stream has been studied by *Godinez et al. (1995)*. Particle size effects (in terms of increasing alkene and impurity conversion with decreasing particle size) were observed over a 0.05 wt. % Pd/γ-Al_2O_3 catalyst with impurity conversion increasing from 25% (original cylinders, 4.5 x 4.5 mm size) to 100% (crushed cylinder, < 0.25 mm). Unfortunately, *Godinez et al. (1995)* do not mention alkene selectivity in their study.

A dependence of selectivity on catalyst particle size was also observed by *Nijhuis et al. (2003a and 2003b)*. Larger catalyst particles exhibited lower selectivity to the alkene, which the authors attributed to mass transfer limitations into the catalyst particle. However, the effect may rather be due to the thicker eggshell observed in the smaller particles.

2.9.2 Metal distribution

In order to minimise the possibility of alkene re-adsorption and subsequent hydrogenation, eggshell catalysts have been utilised in selective hydrogenation. An eggshell catalyst is one in which the active phase lies on the surface of the catalyst particle or forms a thin layer, rather than being distributed throughout the catalyst particle. Re-adsorption would lead to further hydrogenation of the alkene, which is undesired. Consequently, an eggshell structure is preferred when re-adsorption has to be minimised. Figure 2.17 depicts the effect of metal film thickness and pore width on the reactions that occur on an eggshell catalyst. The figure refers to the selective hydrogenation of ethyne. It is observed that in thinner films, once the ethyne is hydrogenated to ethene, the low depth of the film will ensure that the ethene leaves immediately and has no chance to undergo readsorption and be hydrogenated to ethane. In thicker film catalysts the ethene has more time and opportunities for re-adsorption and further hydrogenation. Wide pores of the support assist desorption as well.

Walter et al. (1993) argue that, if an eggshell dispersion was too thick or too active, this would lead to the metal sites of the inner spheres of the shell to be no longer covered by the inhibiting, highly unsaturated species since all of them had been hydrogenated – hence the alkene can react and selectivity will be reduced.

Hall et al. (1994) states that typically modern selective ethyne hydrogenation catalysts have shell thicknesses of less than 300 microns. The loading of palladium is very low (300 ppm). This is due to both the high activity of palladium for hydrogenation and the minimum shell thickness.

A comparative study between eggshell type and catalysts with a uniformly dispersed active metal has been conducted for the selective hydrogenation of isoprene *(Lin and Chou, 1994).* The reaction conditions were 44°C and 30 atm with a H_2/isoprene molar ratio of 2.2 and 10 wt % isoprene in n-heptane. The eggshell type catalyst had a higher selectivity to alkenes and higher activity than the catalyst with uniform dispersion. The higher activity was ascribed to the shorter distance from the pore mouth to the active site of the egg-shell catalyst compared to the catalyst with uniform metal dispersion. The shorter distance also allows less residence time for formation of coke from the oligomerisation of isoprene thus extending catalyst lifetime. The higher selectivity was also ascribed to the shorter distance from the pore mouth to the active site for the egg-shell catalyst compared to the catalyst with uniform dispersion. This allows less residence time for re-adsorption of the alkene and hydrogenation to the alkane.

Arcadia et al. (2001) studied the liquid phase selective hydrogenation of 1,3-butadiene (dissolved in n-hexane) on a commercial Pd/Al_2O_3 eggshell catalyst. The experiments were carried out batch-wise at 40 °C, 0.3 bar hydrogen partial pressure in propane. The catalyst consisted of 0.2 wt. % palladium impregnated on the 230 μm external layer of the alumina catalyst spheres. The results showed strong hydrogen diffusion limitations within the active metal surface layer. The results were fitted to a kinetic model. The model predicted that even for a very thin (10 μm) surface layer, the system is diffusion limited which may be attributed to the fast reaction.

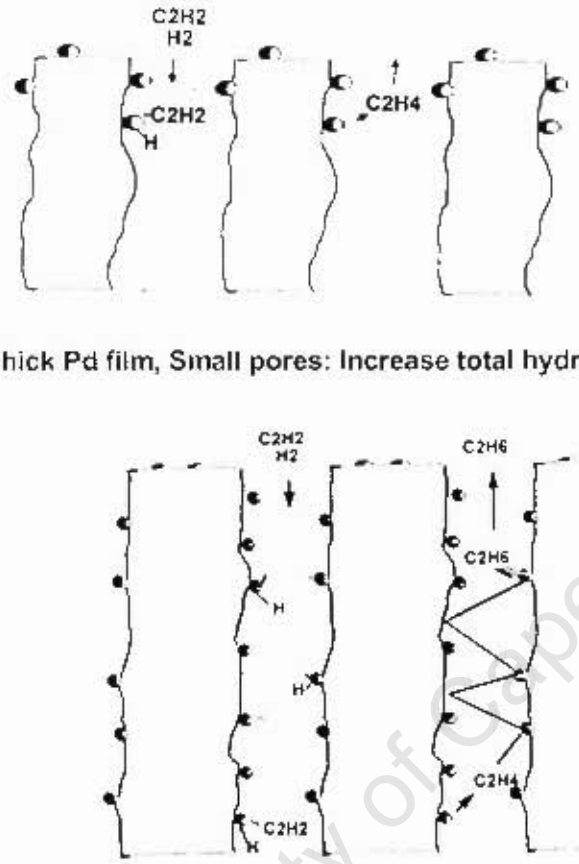

Figure 2.17 Effect of metal film thickness on hydrogenation selectivity (Hall et al., 1994, modified)

The selective hydrogenation of 3-methyl-1-pentyne-3-ol over a silica supported palladium egg-shell catalyst has been investigated by *Nijhuis et al. (2003a and 2003b)*. This is a fast reaction and mass transfer inside the catalyst particle becomes rate limiting. The experiments were carried out batch-wise at 25 °C and atmospheric pressure with solutions of either 0.03 or 0.3 mol/l 3-methyl-1-pentyne-3-ol in ethanol. The same mass of catalyst was loaded onto catalyst particles of different sizes in an eggshell distribution. A gas-inducing stirrer was utilised to ensure saturation of the liquid phase with hydrogen.

2.9.3 Metal dispersion

Changing the particle size of the active metal, changes the dispersion. This changes the percentage of metal atoms exposed to the surface. In case of very small particles this also reduces the co-ordination of the average surface metal atom and, therefore, changes the nature of the chemisorptive bonds of the adsorbed species to the catalyst surface. Very small metal particles (nano-sized) are electron deficient, thus enhancing the adsorption of electron-rich species such as alkynes and alkadienes that will then be more strongly bonded to the metal surface. This may result in the species being too strongly bonded to the surface and hydrogenation activity may decline. The effect has been designated as the "electronic effect" *(Molnar et al., 2001).*

The effect of dispersion is shown graphically in figure 2.18 where the variation of activity for the selective hydrogenation of 1-butyne with metal dispersion for small particles is depicted for several palladium catalysts.

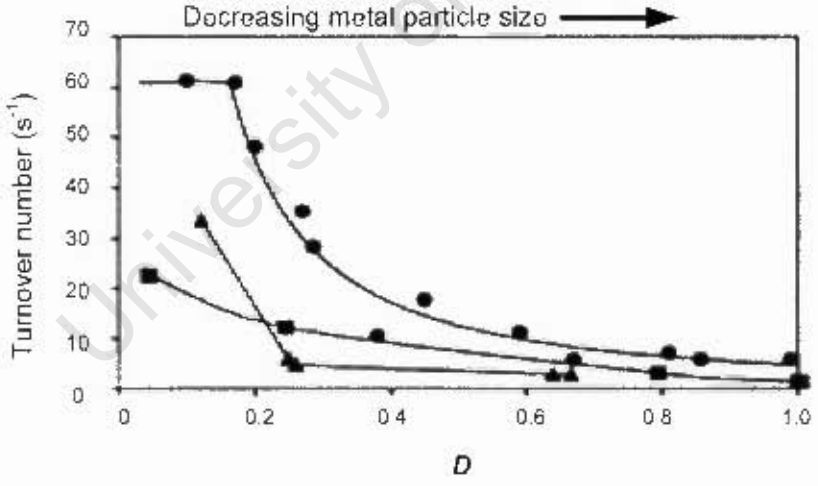

Figure 2.18 Variation of turnover numbers as a function of metal dispersion (D) in the hydrogenation of 1-butyne over Pd/Al_2O_3 (•), Pd/pumice[1] (▲) and Pd/CeO_2 (■) (Molnar et al., 2001, modified)

[1] Pumice is a highly porous amorphous igneous rock consisting mainly of silicon oxide (67-75%) and aluminium oxide (10-20%) with minor amounts of sodium oxide (Na_2O), potassium oxide (K_2O), and calcium oxide (CaO) *(Sax and Lewis, 1989). Molnar et al. (2001)* do not provide the composition of the pumice utilised in the study.

Another example of the effect of dispersion is shown in figure 2.19.

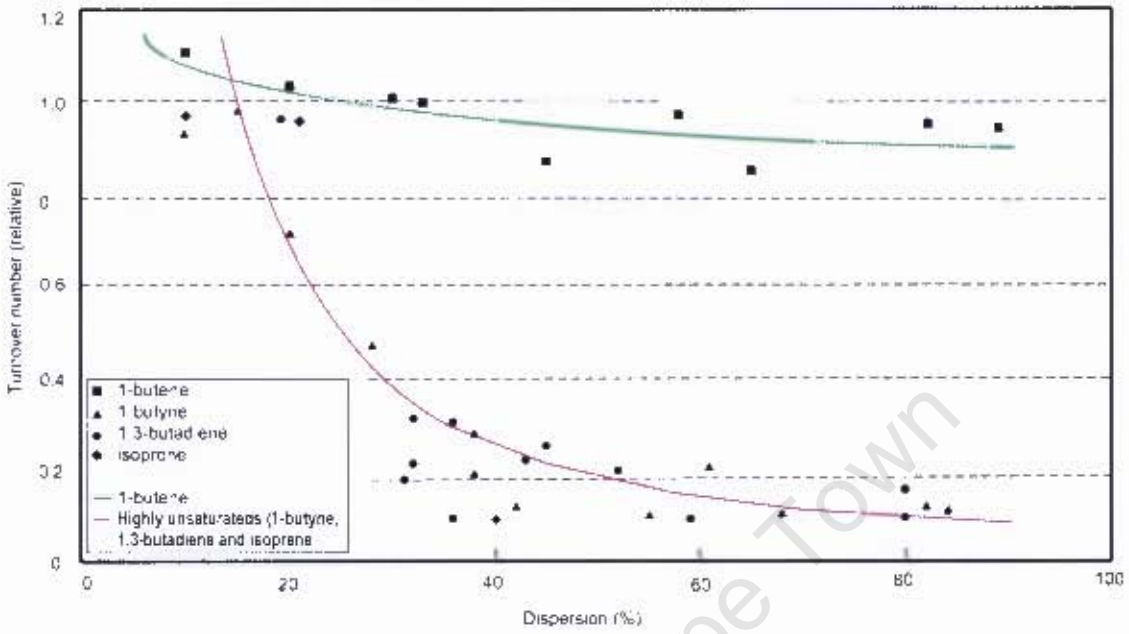

Figure 2.19 Activity of various palladium catalysts (turnover numbers in selective hydrogenation) as a function of palladium dispersion (Walter et al., 1993), no reaction conditions given

1-Butene and various highly unsaturated C_4 and C_5 hydrocarbons have been hydrogenated over various palladium catalysts on different carriers and with different dispersions of the palladium *(Walter et al., 1993).* As soon as dispersion rose above about 30 % it was found that, while the turnover number of 1-butene was relatively unaffected, the highly unsaturated alkenes were much more slowly converted to products. This means that the adsorption of electron rich highly unsaturated alkenes are strongly bound to the electron deficient small palladium crystallites and hence their reaction rates decrease. This means also that palladium based selective hydrogenation catalysts – regardless of the type of carrier – are more selective when their dispersion is low.

Several studies have been carried out by *Boitiaux et al. (1985, 1987a, 1987b)* on the liquid phase hydrogenation of mixtures of 10 mol % of 1-butene, 1,3-butadiene and 1-butyne in n-heptane, dissolved individually, over supported platinum, palladium and rhodium catalysts. For the platinum and palladium

catalysts, it was observed that 1-butyne hydrogenation was sensitive to the metal dispersion, with low activity at high metal dispersions. It was concluded that the 1-butyne undergoes a "multicomplexation" interaction with the metal sties. Two 1-butyne molecules would bond to a single metal site rendering it inactive. This would cause the low reactivity of 1-butyne. At high dispersions, there is a decrease in the average co-ordination number of the metal. This lower co-ordination would allow multicomplexation and, hence, cause lower reactivity *(Boitiaux et al., 1987a, 1987b)*. For the rhodium catalysts, this multicomplexation interaction occurred for 1-butyne and 1,3-butadiene.

The multicomplexation effect was shown to be eliminated on a highly dispersed palladium catalyst by the addition of piperidine *(Boitiaux et al., 1985)*. This was explained by the electron donating effect (Lewis base) of the piperidine.

It appears that this so-called multicomplexation effect is just another name for the metal particle size effect with smaller metal particles being electron deficient leading to strong adsorption of electron-rich species such as 1-butyne (with palladium and alkynes bonding is too strong, so that activity declines) *(Molnar et al., 2001)*. The piperidine addition donates electron density to the active metal atoms, leading to weaker adsorption of the electron-rich alkyne species and consequently higher activity. Thus the addition of piperidine increased the activity for the hydrogenation of 1-butyne.

2.10 The β-palladium hydride phase

Hydrogen interaction with palladium crystallites results in the formation of palladium hydride phases. Two different phases of palladium hydrides can form: a hydrogen-poor α phase (α-PdH) and a hydrogen-rich β phase (β-PdH). This has been confirmed by XRD studies *(Molnar et al., 2001)*. The presence of the β–palladium hydride phase results in increased activity but decreased selectivity of the selective hydrogenation compared to the α phase. It has been shown that

for the selective hydrogenation of ethyne the presence of the β-PdH phase increases the rate of complete hydrogenation to ethane while the absence of the β-PdH phase results in an increase in the ethene selectivity. It has been shown that the presence of the β phase can be eliminated by high metal dispersion, i.e. decreasing palladium particle size *(Bos and Westerterp, 1993).* It has also been shown that the presence of the β-PdH phase can be suppressed by the addition of a second metal *(Coq and Figueras, 2001).* Therefore the high selectivity of highly dispersed palladium catalysts may also be attributed to the absence of the β-PdH phase. However, both increased dispersion and addition of a second metal alter the electronic properties of the metal particles making their surface more electron-deficient, so that this effect may also explain the absence of the hydrogen rich β-PdH phase and the increase in the hydrogenation selectivity.

In the selective hydrogenation of alkynes, the active sites of the catalyst are covered by the alkyne molecules due to their high adsorption strength, whilst hydrogen is adsorbed dissociatively and rather weakly. Under these conditions it is expected that, as the hydrogen adsorbs onto the surface, it immediately reacts with the alkyne and is replaced by another hydrogen atom. Therefore, it is reasonable to suggest that the β-PdH phase may not be able to form on the working catalyst due to insufficient hydrogen availability on the surface *(Molnar et al., 2001).*

In the review by *Molnar et al. (2001)*, several studies regarding the effect of the β-PdH phase have been mentioned but reports have offered contradictory results. High alkene selectivity has even been reported in the presence of the β-PdH phase and in a recent study low ethene selectivity from selective hydrogenation of ethyne was observed in both the presence and absence of a β-PdH phase. It is also speculated that the β-PdH phase forms only on non-selective sites.

In conclusion, it may be summarised that the β-PdH phase has been shown to exist, but at present its effect on hydrogenation selectivity and if it causes an effect at all, has not been satisfactorily demonstrated and understood.

2.11 The effect of excess and gaseous hydrogen

In a study conducted by *McPherson (2003)*, where the selective hydrogenation of various highly unsaturated impurities in 1-hexene were tested over several catalysts, it was noted that at conditions of high space time and at the higher reaction temperatures, the hydrogenation reaction becomes hydrogen limited. It should be noted that *McPherson (2003)* worked in trickle bed mode in the presence of gaseous hydrogen and hydrogen consumption was mainly due to hydrogenation of the 1-hexene. *McPherson's (2003)* results are depicted in figure 2.20, where the rate of hydrogen consumption is plotted against space time. For the less active catalyst, at 51°C, the rate was independent of space time and although conversion increased with increasing space time, the reaction was kinetically controlled. However, at 65°C, the hydrogen consumption rate decreased with increasing space time, suggesting hydrogen limitation. The more active catalyst displayed declining rates at both temperatures. These findings suggest the presence of a hydrogen mass transfer limitation. *McPherson (2003)* attributed this hydrogen mass transfer limitation to reduced hydrodynamic turbulence in the trickle bed reactor at higher space time, i.e. lower linear velocity of the fluid phases, and consequently decreased gas-liquid interfacial area thereby limiting the transfer of hydrogen from the gas to the liquid phase and to the active sites, meaning that hydrogen dissolution in the liquid was mass transfer controlled and below equilibrium.

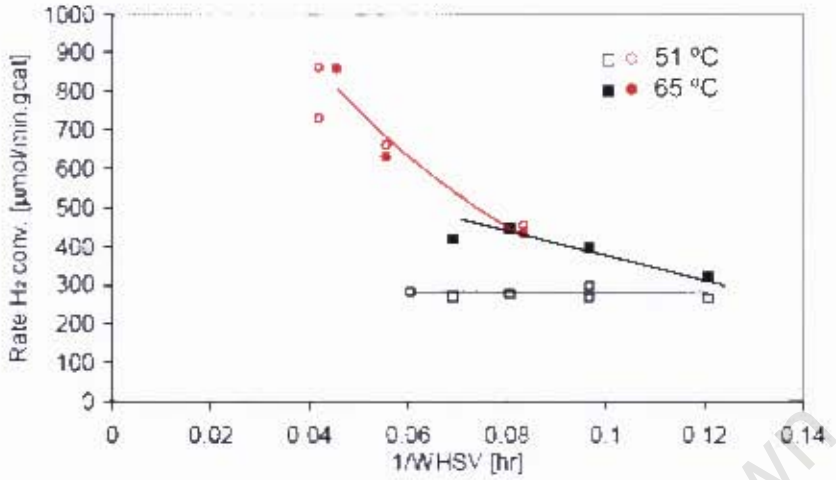

Figure 2.20 Effect of space time on hydrogen consumption rate [□■less active catalyst, ○●more active catalyst, P=15 bar, H_2/Oil=0.2 (molar), WHSV=8.3-10.4 $g_{total\ hydrocarbons}/g_{catalyst}.hr$] (McPherson, 2003)

In the industrial hydrogenative purification of C_2-alkene streams, the stoichiometric molar ratio of hydrogen to ethyne of one is not applied. This is because the catalyst is not 100 % selective to ethene so that a higher ratio is required to obtain complete conversion of ethyne. Also, an increase in hydrogen content accelerates ethyne conversion. This becomes important as the formation of green oil causes a constant decrease in catalyst activity with time-on-stream. Increasing the H_2/ethyne ratio compensates for the deactivation, but results in a decrease in ethene selectivity due to increasing hydrogenation *(Süd-Chemie, 2000).*

The selectivity of hydrogenation of ethyne in ethene over supported palladium catalysts was also shown by *Duca et al. (1996)* to be a function of the H_2/ethyne ratio. At low H_2/ethyne ratio, ethane selectivity did not change with ethyne conversion but did so at high H_2/ethyne ratio. The study did not conclusively show the reason for this phenomenon.

The effect of gas phase hydrogen on the selective hydrogenation of butadiene and butyne in 1-butene was also investigated by *Nierlich and Obenhaus (1986).*

The absence of gaseous hydrogen resulted in higher impurity conversion and a gain in 1-butene.

Brown (2005) conducted a study on the selective hydrogenative purification of 1-hexene in the liquid phase with 1-hexyne as the highly unsaturated impurity. In a series of experiments it was shown that it was either the restriction to a stoichiometric ratio of hydrogen to impurity and/or the absence of gas phase hydrogen in the reactor that resulted in specificities (see section 4.5.4.4) of approximately 100. Excess hydrogen was regarded as the hydrogen above that required to hydrogenate all of the highly unsaturated impurities to 1-hexene, whilst gaseous hydrogen was hydrogen that was not dissolved in the liquid reaction mixture. The absence of gaseous hydrogen in the reactor was assumed to have been achieved by completely dissolving the hydrogen in a hydrogen dissolution vessel before reaching the reactor and limited hydrogen supply as determined by hydrogen solubility in 1-hexene.

It has been concluded that the absence of gas phase hydrogen, naturally, avoids any limitation of hydrogen mass transfer from the gas to the liquid phase, and thus results in improved conversion of impurities *(Brown, 2005).*

2.11.1 Hydrogen solubility in 1-hexene

It has been shown by *Nierlich and Obenhaus (1986)* and *Brown (2005)* that the absence of gaseous hydrogen in the catalyst bed results in high specificity. Therefore it is necessary to ensure that all the hydrogen fed is dissolved in the liquid phase under reaction conditions. In order to calculate the solubility of hydrogen in 1-hexene, a simulation was undertaken using Aspen Plus (appendix A). The liquid was assumed to consist of 1-hexene only. This assumption is valid since the technical feed to a possible selective hydrogenation reactor (and, consequently, any suitable model mixture) consists of 98+ mol% 1-hexene, whilst the remaining compounds are also C_6's. The results of the simulations are presented in figure 2.21. The solubility of hydrogen is shown as a function of

temperature and pressure. Hydrogen solubility in 1-hexene is low at atmospheric pressure and low temperature and increases with both temperature and pressure. At 30 bar and 60 °C, which was the standard operating pressure and temperature applied in this study, approximately 2 mol % of hydrogen can be dissolved in the liquid phase.

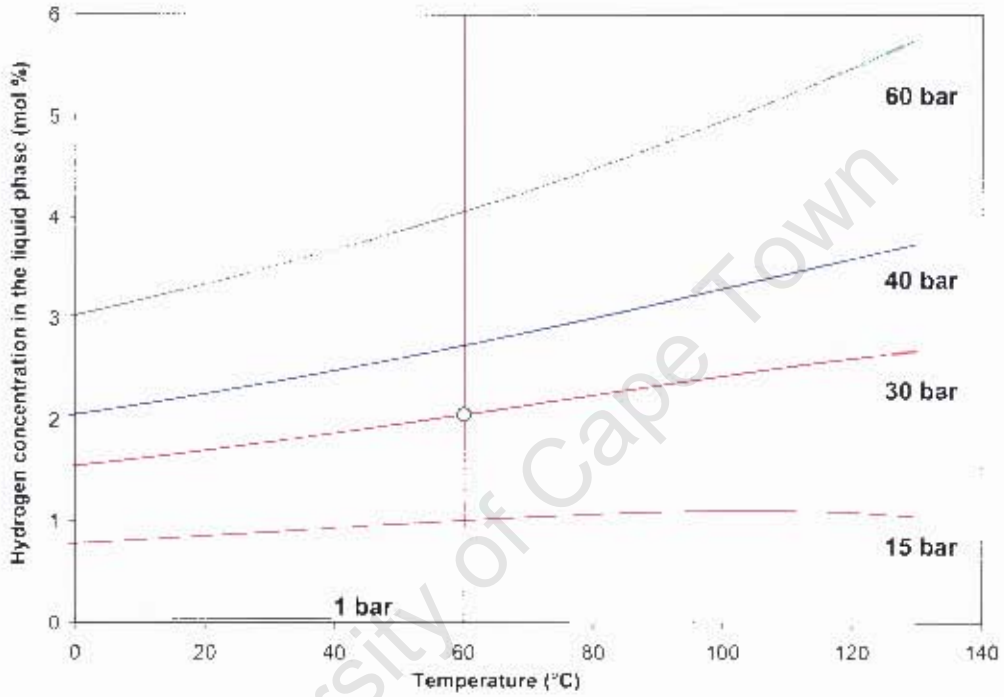

Figure 2.21 Solubility of hydrogen in 1-hexene as a function of temperature and pressure (Aspen Plus simulation, based on thermodynamic data from the Aspen data base). (The vertical line marks the reaction temperature applied in this study. The open circle marks the standard operating conditions)

2.12 The role of co-adsorbents

Carbon monoxide is commonly co-fed in commercial processes for the selective hydrogenation of ethyne in C_2-streams *(Süd-Chemie, 2000)*. CO acts as an inhibitor, decreasing the activity but increases the selectivity by preventing over-hydrogenation. CO competes for the active sites. CO adsorption strength is greater than ethyne adsorption strength which in turn is greater than ethene adsorption strength *(Tiedtke et al., 1994)*. Due to these differences in relative

This hypothesis is supported by *Boitiaux et al. (1993)*, who added piperidine to an alumina supported palladium catalyst for the selective hydrogenation of 1-butyne, 1,3-butadiene and isoprene and found increased hydrogenation activity and selectivity. The convincing result is shown in figure 2.22 for the selective hydrogenation of 0.3 vol % 1-butyne in 1-butene over a Pd/Al_2O_3 catalyst in a batch reactor in the presence or absence of trace concentrations of piperidine in the feed (0.25 vol %).

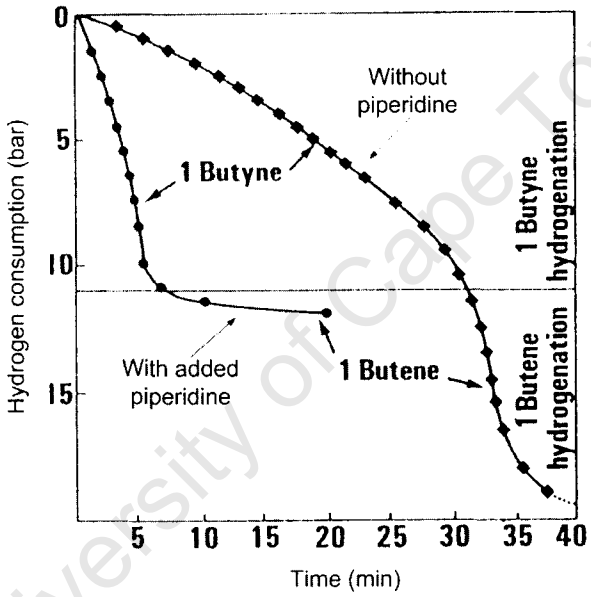

Figure 2.22 Hydrogen pressure drop (to visualise the hydrogen uptake) as a function of residence time for batch-wise 1-butyne hydrogenation with and without piperidine being present. The solid line represents the calculated hydrogen pressure for the stoichiometric conversion of 1-butyne to 1-butene. (0.3 vol % 1-butyne in 1-butene, 0.25 vol % piperidine, 0.33 % Pd/Al_2O_3 of 37 % dispersion, 19 °C, initial pressure 20 bar) (Boitiaux et al, 1993, modified)

In the presence of piperidine the initial hydrogen uptake is high. Very rapid hydrogen consumption occurs up to the stoichiometric value of hydrogen consumption through the conversion of 1-butyne to 1-butene. Then the rate of hydrogen consumption slows down indicating the slow hydrogenation of

1-butene. The increase in activity and selectivity is interpreted as a destabilisation of the π-donation character of both the strongly bonded alkyne and the less strongly bonded alkene (product) induced by the strongly donating piperidine, which increases the electron density of the palladium sites. Thus piperidine limits the self-inhibiting effect of 1-butyne adsorption on its own hydrogenation and significantly weakens the adsorption of 1-butene leading to a repulsion of the product from the surface.

A Cu/SiO_2 catalyst modified with n-butylamine *(Sarkany, 1997)* displayed a lower degree of total hydrogenation and alkene isomerisation compared to an unmodified catalyst whilst still maintaining high activity for selective hydrogenation for 1,3-butadiene *(Sarkany, 1997).* The higher selectivity of the modified catalyst has been attributed to FHA (firmly held adsorbed species) formed from the n-butylamine which prevents the adsorption of the 1-butene once the alkadiene has been depleted. 1,3-Butadiene on the other hand had a higher adsorption strength and was able to 'push away' the FHA *(Sarkany, 1997).*

2.13 The effect of oligomer formation

Hydrogenation of unsaturated hydrocarbons, in particular highly unsaturated aliphatic hydrocarbons, leads to the formation of various oligomers as by-products. In the selective hydrogenation of ethyne, three types of oligomers have been found. There are the gaseous C_4-C_6 oligomers, the liquid heavy oligomers (known as green oil), and the solid polymers which are regarded as coke/carbon deposits. The coke deposits remain on the catalyst surface until the catalyst is regenerated with steam and air. However, the presence of all of these oligomers in the reaction mixture decreases activity and selectivity. The coke deposits also decrease catalyst lifetime *(Kochloefl, 1995).*

1,3-Butadiene has been postulated as a precursor for oligomers which is formed from the dimerisation of ethyne *(Süd-Chemie, 2000).* A drastic reduction in green oil content is obtained by the addition of a second metal. A 66 % reduction in green oil formation over a silver promoted industrial palladium catalyst has been asserted, compared to the non-promoted catalyst *(Süd-Chemie, 2000).* It has been postulated that the second metal dilutes the palladium sites, diminishing the amount of 1,3-butadiene formed *(Süd-Chemie, 2000).* A similar inhibiting effect is observed when CO is added. However, it has been observed that CO is incorporated into the oligomers resulting in carbonyl compounds formation *(Kochloefl, 1995).* The promoted catalysts also produce shorter chain oligomers which are easier to remove, which enables longer cycle times.

In the review by *Molnar et al. (2001)*, it is stated that hydrogen is required for oligomerisation and that in the absence of hydrogen no oligomers are formed. A mechanism involving a vinyl radical (such as species 3 in figure 2.12) has been proposed for the formation of oligomers, though this is still being debated in the literature. It has been observed that the working palladium sites are covered by a carbonaceous layer, but the effect of this layer upon activity and selectivity is not clear.

Maetz and Touroude (1997) studied the modification of surface activity by adsorbed hydrocarbon species on supported palladium and platinum catalysts for the selective hydrogenation of 1-butyne. They found that the selectivity for 1-butene is regulated by a hydrocarbon overlayer, composed of 2-butyne species. This layer is equilibrated with the reaction intermediates. The layer does not form if the 1-butene intermediate is rapidly hydrogenated to butane.

Ponec et al. (1990) (cited in Molnar et al., 2001) attribute the effect of the hydrocarbon layer to ensemble size. Large ensembles of active metal sites are able to form multiply bonded species, which leads to ethane formation. Coke deposition breaks up these large ensembles and dilutes the active sites.

The formation of a hydrocarbon overlayer has even been made responsible for the selective hydrogenation of propyne over alumina supported palladium and platinum catalysts *(Kennedy, 2004).* The hydrocarbon overlayer was attributed as the active site for propene formation.

A study by *Koeppel et al. (1994)* utilising a Cu/SiO_2 catalyst for the gas phase hydrogenation of 1-butyne and 1,3-butadiene revealed high 1-butene selectivity. Catalyst deactivation due to the formation of oligomers was pronounced, but the authors did not attribute the high 1-butene selectivity to the formation of these oligomers.

Sarkany (1997) studied the selective hydrogenation of 1,3-butadiene on Co/Al_2O_3 showing the presence of surface hydrocarbonaceous materials but regarding it as competition for the active sites.

Sarkany et al. (2002) observed the formation of a surface hydrocarbonaceous layer that was removed under high hydrogen excess but which resulted in low selectivity. It has been postulated by *Borodziński (1997, 2000) (cited in Molnar et al., 2001)* that the hydrocarbon layer decreased hydrogen availability and that steric hindrance, caused by crowding of the surface, repels the alkene, which prevents further hydrogenation. However this explanation does not suffice since steric hindrance would also decrease adsorption of ethyne.

Asplund (1996) studied the selective hydrogenation of ethyne in ethene over a Pd/Al_2O_3 catalyst. The results indicated that the formation of carbon deposits decreased diffusivity by blocking catalyst pores. This results in longer residence time of ethene in the pores, leading to greater probability of readsorption and further hydrogenation.

2.14 Effects of mass transfer control

Effects of mass transfer control were observed in selective hydrogenation. Some of the effects have already been addressed in the previous sections.

2.14.1 Internal mass transfer control

This aspect was extensively discussed in sections 2.9.1 and 2.9.2 in the context of catalyst particle size, pore size and metal distribution over the catalyst particle. These sections showed the need for eggshell type catalysts to improve intermediate selectivity that is to prevent the alkene, the desired intermediate of alkyne and alkadiene hydrogenation, from readsorption and total hydrogenation to the alkane in the catalyst pores. Coking may cause pore blockage, reduce diffusivities and thus also increase internal mass transfer limitation and thus the probability of alkene readsorption *(Asplund, 1996).*

2.14.2 Hydrogen mass transfer limitation on gas/liquid surface in trickle phase operating mode

McPherson (2003) studied selective hydrogenation of highly unsaturated impurities in 1-hexene in a reactor operated in trickle mode with gaseous hydrogen present. Specificities reported were very low, less than 3, and conversion of 1-hexene was in the range of 10-20% and higher. The latter, in combination with the limited hydrogen dissolution capacity of the 'oil' phase, figure 2.21, led to the depletion of dissolved hydrogen. Hydrogen supply eventually became controlled by mass transfer through the gas-liquid interface (section 2.11 and figure 2.20) as concluded by *McPherson (2003).*

However, as stated by *Brown (2005),* in the absence of gas phase hydrogen, as recommended (section 2.11), limitation of hydrogen mass transfer from the gas to the liquid phase is, naturally, no longer possible.

2.14.3 External mass transfer control

At low linear velocities, shear forces in the fluid phase in the catalyst bed are weak and flow patterns may even be laminar. This results in comparatively thick stagnant layers of fluid surrounding the individual catalyst particles and this is a significant diffusion barrier for reactants and products between the fluid phase and the surface of the catalyst particle. Consequently, the mass transfer coefficient may become much smaller than the reaction rate constant, so that the rate of mass transfer to the surface limits the overall rate of reaction *(Fogler, 1999).*

For conversion in a fixed bed reactor without external mass transfer control, such as found in a differential reactor (packed bed tubular reactor), there is no effect of fluid phase linear velocity on reaction rate. Hence, conversion (X_r) is proportional to the reciprocal of space velocity (SV) such that $X_r \propto \frac{1}{\mathrm{SV}}$.

However, under external mass transfer control the rate of reaction is controlled by the mass transfer coefficient, which is proportional to the square root of the linear velocity of the fluid phase. Hence, the reaction rate under external mass transfer control (*-r*) is proportional to the square root of the space velocity *(Fogler, 1999)*, $-r \propto \sqrt{\mathrm{SV}}$. Consequently, due to these antagonistic effects, a decrease of space velocity will only have a small increasing effect on impurity conversion.

To evaluate external mass transfer limitation, conversion versus space velocity must be determined with different amounts of catalyst and, correspondingly, different volumetric flow rates and linear velocities but at the same space velocities. Coincidence of conversion values at the same space velocities indicates the absence of external diffusion limitation while differences (lower conversion at the lower flowrate) indicates external mass transfer control.

In a study on selective hydrogenation of a simulated C_2/C_3 steam cracker product over two commercial Pd-Ag/Al_2O_3 catalysts in a laboratory scale fixed bed

reactor this was indeed observed *(Godinez et al., 1995). Godinez et al. (1995)* obtained convergence of conversion vs. W/F curves with different catalyst systems only at "extremely" high flows, suggesting important external gradients over practically the whole range of experiments carried out (figure 2.23).

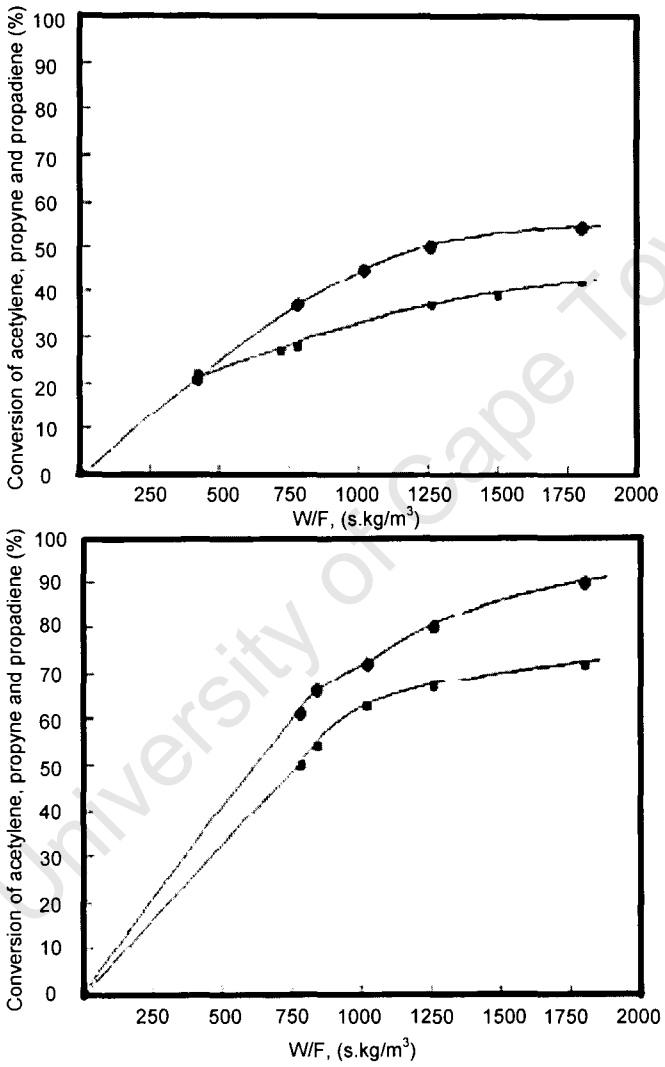

Figure 2.23 Overall conversions vs. W/F obtained for the selective hydrogenation of a simulated C_2/C_3 steam cracker product in a laboratory scale experiment over two different Pd-Ag/Al_2O_3 catalysts of cylindrical particle shape of 4x4 mm (top graph) and 4.5x4.5 mm (bottom graph). The conditions utilised were 80°C, gas phase, with hydrogen/unsaturated hydrocarbon molar ratio = 15. The top curve in each graph represents 15 g of catalyst and the bottom curve of each graph represents 7.5 g of catalyst (Godinez et al., 1995, modified)

2.15 A strange effect of space velocity

In a patent about alkadiene removal from long chain alkene fractions over 'preferentially' palladium catalysts, *Himelfarb and Bolinger (2002)* point out the following:

"Surprisingly, the catalysts preferably are used in fixed bed trickle flow reaction mode at low feed flow. Persons of ordinary skill in the art would expect that a relatively long exposure time between the feedstock and the catalyst in a trickle flow mode would result in more hydrogenation and an undesirably high production of paraffins in the product. The longer the feedstock is exposed to the catalyst, the more selective the process is to the production of alkenes. This is particularly true at a low gas flow and when the level of hydrogen in the reaction gas is limited, preferably to about 2 to about 6 vol. %, with the remainder being an inert gas, preferably nitrogen. In other words, the longer the exposure to the catalyst and to a reaction gas having a limited hydrogen content, the higher the conversion of dienes, and the lower the yield of paraffins."

No suggestions are made about the reasons for this 'surprising' result.

It should be noted that the patent by *Himelfarb and Bolinger (2002)* refers to an "olefin feedstock" or a "predominantly linear olefin feed" but not specifically to a 1-olefin (1-alkene) feedstock. However other passages of the text mention hydroformylation of these 'olefins' to form "an alcohol" and that "over 80 % of the alcohol molecules are linear primary alcohols'. This indicates towards an olefin feed consisting of mostly 1-alkenes and that these 1-alkenes survive this long exposure time to the catalyst.

If applicable on selective hydrogenation of highly unsaturated impurities in 1-alkene streams, this should improve the specificity of the reaction.

2.16 Overview of literature findings

The use of linear 1-alkenes as polyethylene co-monomers is a fast growing application of 1-alkenes with several of the world's largest producers of petrochemicals embarking on projects to increase production of these valuable commodities to meet with this increased demand. In addition to the 'classical' ethene oligomerisation processes, new resources have been opened up during the last decade and new technologies have been developed. An example is Sasol, who are extracting 1-alkenes from the product of high temperature Fischer-Tropsch synthesis. Sasol entered the 1-alkene market only in 1994 (chapter 1) and has now become a global player. Another example is the Q-Chem plant which started up in 2002 in Qatar, where ethene is selectively trimerised to 1-hexene (section 2.1.2.1.3.2). New plants aim also to make better use of lower value refinery streams such as at Sasol Synfuels in Secunda where a third 1-octene train is being commissioned utilising hydroformylation of 1-heptene, a stream otherwise added to the petrol pool (section 2.1.2.4).

Continuous, 1-stage ethene oligomerisation produces a Schulz-Flory type oligomer carbon number distribution of even-numbered linear 1-alkenes with selectivity maximum, naturally, at C_4, while discontinuous, 2-stage ethene oligomerisation produces a somewhat narrower cut with a Poisson distribution and an adjustable maximum of the carbon number distribution higher than C_4. However, the market for the lighter linear 1-alkenes C_6 and C_8 for use as co-monomers is growing faster than that for the heavier fractions (section 2.1.1), so research aims to develop processes to 'selectively olgimerise' ethene to specific carbon number products, enabling companies to increase production of the more valuable lighter linear 1-alkenes. A great success of this type of research is the aforementioned 1-hexene selective Q-Chem ethene trimerisation plant, the only one of its kind in the world (section 2.1.2.1.3.2). Sasol Technology has also developed a technique for selective ethene trimerisation (section 2.1.2.1.3.2) and is developing a process to selectively oligomerise ethene to

1-octene. If successful, it will be a world first for selective ethene tetramerisation (section 2.1.2.1.3.3).

Other carbon number selective processes developed are the dimerisation of 1,3-butadiene to 1-octene by the OXENO process (section 2.1.2.2), and the hydroformylation of 1-heptene to 1-octene by Sasol (section 2.1.2.4).

Light alkene streams are mainly produced by steam cracking (pyrolysis) of light refinery streams, ethane or condensates from natural gas, with the product distribution dependent on the starting material. Another route to alkenes is catalytic cracking, with such a process being more selective to medium carbon number alkenes than the pyrolysis process. High temperature Fischer-Tropsch synthesis is another process that produces mainly alkenes. All of these processes produce, in addition to the desired alkenes, unwanted harmful components, such as alkynes and alkadienes. In the ethene streams, ethyne is contained as a by-product. Though present in a few percent only in the steam cracker product and much less in other olefinic product streams, alkynes and alkadienes would have a detrimental effect on certain ethene oligomerisation catalysts and their removal is essential (section 2.3).

In the downstream processing of the C_4 alkene stream, alkadienes act as coke precursors which decrease catalyst lifetimes. An example at the Sasol Synfuels complex is the C_4 catalytically cracked gas which must be alkadiene free for the downstream catalytic polymerisation process (section 2.3.4.3). From C_5 alkene streams, which are blended into the petrol pool, alkadienes must also be removed since they are gum precursors.

The process of selective catalytic hydrogenation is utilised for this purpose. The aim of selective hydrogenation of alkene streams is to selectively hydrogenate the highly unsaturated impurities, such as alkadienes and alkynes to the respective alkene, or at least without hydrogenating much of the alkene to the

alkane. In selective hydrogenation of ethyne in ethene rich streams, the process is able to reduce ethyne to the ppm level from initial concentrations of a few percent (section 2.3). The process is conducted at moderate conditions over a heterogeneous catalyst with hydrogen in slight excess of the stoichiometric amount required to hydrogenate all the impurities to the alkene. Commercial catalysts for selective hydrogenation are mainly supported palladium catalysts (section 2.6). The most commonly utilised support materials are alumina, silica and titania (section 2.8).

The preference for alkyne hydrogenation over a supported palladium catalyst is due to the stronger adsorption of the alkyne on the active metal site compared to the alkene due to the strong interaction of the π-electrons in the highly unsaturated compound with the electron deficient palladium surface. The alkyne will, therefore, be preferentially hydrogenated to the alkene until the alkyne concentration is sufficiently low to allow alkene adsorption and hydrogenation (section 2.5.3).

However, alkyne adsorption on the palladium surface is so strong that it results in self inhibition and thus low catalyst activity and selectivity. Donating electron density to the palladium by adding a second metal with electron donor properties, preferentially the group 1B element silver, moderates adsorption strength and improves activity and selectivity (section 2.7). It was found that organic compounds with electron donor properties, added in low concentrations in the feed, such as basic nitrogen compounds, act in a similar manner (section 2.12).

CO is commonly utilised as a co-adsorbent in the selective hydrogenation of ethyne in ethene rich streams. CO has an intermediate adsorption strength between ethyne and ethene so that when all or most of the ethyne is hydrogenated the CO occupies the active metal sites preventing the adsorption and hydrogenation of ethene resulting in higher selectivities (section 2.12).

A problem encountered in the purification of heavier 1-alkene streams is that of isomerisation of linear 1-alkenes to linear internal alkenes, which is not encountered in purification of lower alkene streams such as in ethene streams. This is negated by the use of non-acidic supports (section 2.8) and for the addition of a second metal to the supported palladium catalyst. It is widely believed, that this metal addition dilutes the active metal sites so that there is no close proximity of several active sites as required for double bond isomerisation (section 2.7). A commonly utilised commercial catalyst for such an application is Pd-Ag/Al_2O_3.

Since selective hydrogenation of the highly unsaturated compound should stop at the intermediate alkene and not continue to the alkane, internal mass transfer control effects must be avoided. Consequently, selective hydrogenation catalysts are designed as eggshell catalysts with an extremely thin surface layer of active metal (sections 2.9.1, 2.9.2, 2.14.1 and 2.14.2).

High metal dispersion worsens catalyst performance, reinforcing adsorption strength and self-inhibition of the hydrogenation of the alkyne due to the increasing electron deficit on the surface of very small palladium crystallites (section 2.9.3) and thus too strong adsorption of the alkyne results in self-inhibition.

Reaction rate laws of alkyne hydrogenation are first order in hydrogen and zero order in alkyne, which is due to the strong adsorption of the latter (section 2.5).

In order to quantify the quality of selective hydrogenation, specificity was defined as the ratio of the removal of the highly unsaturated impurity to the loss of the alkene (section 2.5.5).

The hydrogenation of heavier linear 1-alkene streams is conducted in the liquid phase. It has been shown that the absence of gas phase hydrogen results in

higher alkene specificity with higher impurity conversions (section 2.11). It was shown in studies of the liquid phase selective hydrogenation of highly unsaturated impurities (1-butyne and 1-hexyne) in the selective hydrogenative purification of 1-butene and 1-hexene, respectively, that avoiding excess hydrogen resulted in higher conversion of impurity with lower loss of 1-alkene (sections 2.11 and 2.11.1). Excess hydrogen was regarded (i) as more hydrogen than is required to hydrogenate all the highly unsaturated impurity present to 1-alkene or (ii) as gaseous hydrogen that was not dissolved in the liquid reaction mixture.

It has been shown that in lab scale reactors, due to the low linear velocities in these small vessels, external mass transfer control occurs, affecting the results (section 2.14.3).

Selective hydrogenation also leads to the formation of oligomers. The liquid, a dissolved oligomer fraction is known as "green oil" whilst the solid polymers are formed as coke deposits on the selective hydrogenation catalyst. These plug the pores and are only removed upon catalyst regeneration (section 2.13). The presence of this oligomeric material leads to lower selectivity. In the selective hydrogenative purification of ethene, it has been postulated that the dimer, 1,3-butadiene, is an oligomer precursor. The addition of a second metal to the catalyst has been shown to decrease oligomer formation by dilution of active metal sites preventing the formation of 1,3-butadiene (section 2.13).

3 OBJECTIVES OF THIS STUDY

Linear 1-alkenes, for example 1-hexene, are produced either by ethene oligomerisation or are recovered from Fischer-Tropsch or other streams. Despite a high purity (> 99 mol %) of the final 1-hexene products, trace components are typically still present in these feedstocks, which, depending on the production process, may most likely include multiply unsaturated hydrocarbons such as alkadienes and alkynes. Specific types of alkene polymerisation catalysts may be deactivated by these trace impurities, and thus their removal is vital. Selective catalytic hydrogenation has been proposed as a possible means of removal of these highly unsaturated impurities.

Industrially, selective hydrogenation over Pd/Al_2O_3 and $Pd\text{-}Ag/Al_2O_3$ catalysts is utilised to remove the highly unsaturated impurities from the C_2-C_5 alkene and pyrolysis gasoline streams of a steam cracker product. The aim in this work was to selectively remove trace amounts of 1-hexyne, one of the aforementioned types of impurities, from a 1-hexyne / 1-hexene model mixture without double bond isomerisation of the 1-hexene or hydrogenation to n-hexane.

Specificity, the ratio of removal of an impurity to the conversion of the 1-alkene (to either internal alkenes or the n-alkane) has been defined as a measure of catalyst performance *(McPherson, 2003)*. Previous studies have shown a $Pd\text{-}Ag/TiO_2$ catalyst exhibits high hydrogenation activity and high specificity, the latter resulting from use of a support of low acidity, the catalyst's bi-metallic composition and specific reaction conditions *(McPherson, 2003; Brown, 2005)*.

It has been found that high specificity may be obtained under conditions of liquid phase operation, due to either a low hydrogen to impurity ratio (around 1:1 molar with respect to impurity hydrogenation to the corresponding 1-alkene) and/or the addition of a hydrogen dissolution vessel upstream of the reactor in order to avoid the presence of gaseous hydrogen in the catalyst bed *(Brown, 2005)*.

Hence the following hypothesis is proposed:

With the appropriate conditions it is reasonable to develop a process of selective hydrogenation for the purification of 1-hexene streams that has the potential of successful industrial application.

The specific aims of this study are:

- To improve the accuracy of the gas chromatographic analyses.
- To verify the balance of hydrogen in the system.
- To develop a set-up that allows operating of hydrogenation in liquid phase without gas phase hydrogen being present in the reactor.
- To develop a method that allows determining whether gas phase hydrogen is present in the reactor at reaction conditions or not.
- To determine the controlling factor for the high specificity obtained by *Brown (2005)*, either if a stoichiometric amount of hydrogen to impurity has to be utilised or if it is the absence of gaseous hydrogen in the reactor.
- To determine whether external mass transfer limitations play a role or not.
- To achieve higher impurity conversions than *Brown (2005)* by the addition of a second hydrogen feed line and dissolution vessel reactor stage.
- To determine whether high specificity may still be obtained at higher impurity conversion than achieved by *Brown (2005).*

4 EXPERIMENTAL PROCEDURES

4.1 Catalyst of choice

The study by *Brown (2005)* suggests that a bimetallic palladium-silver catalyst, supported on titania, Pd-Ag/TiO_2, may be applied successfully for the hydrogenative purification of 1-hexene. The catalyst utilised was a laboratory specimen obtained from Süd-Chemie with the designation T4299. It has not been designed or optimised by Süd-Chemie for purification of 1-hexene via selective hydrogenation, but rather chosen by *Brown (2005)* on the basis of a need for a bi-metallic palladium catalyst on a non-acidic support.

The catalyst particles were of an egg-shell type, meaning that the loaded metals are deposited within a thin layer right below the geometric surface of the catalyst particle. The titania support was P25, a commercial material manufactured by Degussa [comprising 10 nm primary particles, aggregated into 100 nm clusters then 10 μm agglomerates, and finally, pressed to cylindrical tablets, 4.5 mm in diameter *(Degussa AG, 2003)*. These tablets were then loaded with the metals *(Süd-Chemie, 2003)*. The catalyst composition and appearance of particles is detailed in table 4.1.

Table 4.1 Catalyst composition and appearance of particles *(Süd-Chemie, 2003; McPherson, 2003)*

Shape of catalyst particle	Cylindrical
Catalyst particle diameter	4.5 mm
Catalyst particle length	4.5 mm
Average weight of catalyst particle	0.15 g
Catalyst support	Titania
Base metal	0.18 wt% Pd
Promoter metal	0.13 wt% Ag
Mean metal particle diameter	2-5 nm (calculated from transmission electron microscopy) *(McPherson, 2003)*
Mean metal particle diameter	3 nm (calculated from CO chemisorption) *(McPherson, 2003)* [a]
Metal dispersion	41% (calculated from CO chemisorption) *(McPherson, 2003)* [a]
Average metal surface area per unit mass of catalyst	37 m^2 / g (calculated from CO chemisorption) *(McPherson, 2003)*[a]

[a] According to *McPherson (2003)*, CO chemisorption titrated the total metal surface (Pd and Ag) and did not distinguish between the two different metals. Since silver is considered as an inert diluent or structural and chemical promoter of the palladium (see section 2.7), the calculated mean particle diameter, metal dispersion and average metal surface area per unit mass of catalyst do not correspond to that of the active surface of the catalyst.

4.2 Feedstocks

The 1-hexene utilised in this study was an industrial product of co-polymer quality with a purity of > 99.2 mol %. The 1-hexene was supplied in a cylinder with two ports, one for nitrogen pressurising and one fitted with a dip tube for supply of the liquid.

The liquid and gaseous compounds used as co-feeds and auxiliaries, with their suppliers and purities, are detailed in table 4.2. 1-Hexyne was utilised as a model impurity compound for this study. The 1-hexyne was utilised to represent a type of highly unsaturated impurities that is most likely present in a 1-hexene stream Molnar et al., 2001), and must be removed in the final stage of purification to polymer grade. As such, this 1-hexyne was added in small quantities to the bulk 1-hexene feed. The concentrations utilised were 0.5 and 1.0 mol %, of 1-hexyne in 1-hexene. In initial runs, this feed mixture was combined by volume, but in later runs the more accurate method of preparation by mass was employed (see appendix C for the feed preparation method). Feed mixtures were stored in a refrigerator in order to prevent vaporisation of the volatile feed constituents.

The gaseous feedstocks and auxiliaries were provided via the house line. These were hydrogen and nitrogen.

To each product sample obtained from the experimental test apparatus, an internal standard mixture was added. This mixture consisted of cyclohexane and 2-methyl pentane (see section 4.5.3).

adsorption strengths, once the ethyne is hydrogenated to ethene, the desorption of ethene is encouraged due to CO adsorption. CO further inhibits the readsorption of ethene, which decreases the possibility of further hydrogenation. Hence, co-fed CO increases ethene selectivity. In the absence of CO, selectivity is high until high conversion of ethyne is obtained since at high ethyne conversions the surface concentration of ethyne drops, enabling adsorption of ethene leading to further hydrogenation. The addition of CO hinders ethene adsorption at low ethyne surface concentrations *(Tiedtke et al., 1994).* However, due to the reduced activity, higher operating temperatures are required (*Süd-Chemie, 2000).* Industrially, in back-end hydrogenation, up to 3 ppm vol CO is added, with as little as 0.5 ppm enhancing the selectivity *(Süd-Chemie, 2000).* In the front-end application, up to 1000 ppm vol CO is added *(Molnar et al., 2001).* In heavier alkene streams, CO may also have a site diluting effect, preventing the formation of large ensembles of active metal atoms required for isomerisation.

In the review by *Molnar et al. (2001)*, it was noted that several recent studies have claimed that the selectivity enhancement effect of CO was not due to blocking of adsorption sites for ethyne and ethene, but rather by competition between CO and hydrogen for active sites. This was confirmed with deuterium experiments, which revealed that the addition of CO decreased the formation of surface vinyl species which was explained by decreased hydrogen concentration on the catalyst surface *(Park and Price, 1991, cited in Molnar et al., 2001).* Although this hypothesis would explain lower hydrogenation conversion, it does not account for the higher ethene selectivity obtained via CO addition.

CO addition has also been studied in the context of the selective purification of heavier alkene streams. A study by *Nierlich and Obenhaus (1986)* revealed that the addition of CO to the feed for the selective hydrogenation of butadiene and butyne dissolved in 1-butene resulted in higher impurity conversion and a gain in 1-butene.

In the mechanism proposed by *McGown et al. (1978)*, two types of sites are postulated to be involved in the hydrogenation of ethyne dissolved in ethene. On the one type of site, ethyne is selectively hydrogenated to ethene. On the other type of site, ethene is hydrogenated even in the presence of high ethyne concentrations. The effect of CO was attributed to its competition with ethene on the latter type of sites. It was also found that increasing CO concentrations decreased oligomer formation which was attributed to decreased hydrogen surface concentrations.

In a recent study by *Brown (2005)* it was shown that the addition of low concentrations of CO and ethanol, as competitive adsorbates to 1-hexene, did not effect a noticeable specificity increase. However, in the study a bimetallic Pd-Ag/TiO_2 catalyst had been utilised. It was postulated that catalytic site 'dilution' i.e. degradation of ensembles of active metal sites, had already been achieved by adding the second metal, silver, contained in the bi-metallic catalyst.

Several other additives have been studied in selective hydrogenation applications. In all of the examples discussed below a basic organic nitrogen compound was added, i.e. a compound that can provide additional electron density by the lone, basic electron pair on the nitrogen atom.

In early studies, quinoline was added to the Lindlar catalyst (lead poisoned palladium on a $CaCO_3$ support) *(Lindlar and Dubuis, 1973, cited in Molnar et al., 2001).* It was postulated that the addition of this nucleophilic i.e. electron rich species, increased electron density on the metal surface which consequently decreases the interaction of electron rich alkynes and alkadienes with the metal. This decreased interaction would also lead to increased desorption of the intermediate alkene formed from hydrogenation of the alkyne, resulting in a higher selectivity *(Molnar et al., 2001).* The alkene, also being electron-rich, will also experience a decreased interaction with the metal surface due to the addition of the nucleophilic species, decreasing the possibility of re-adsorption and further hydrogenation, increasing the alkene selectivity.

Table 4.2 Liquid and gaseous compounds used as co-feeds and auxiliaries, their suppliers and purities

Compound	Supplier	Purity
1-Hexyne	Aldrich	97 mol %
Cyclohexane	Fluka	>99 mol %
2-Methyl pentane	Aldrich	97 mol %
Hydrogen	Air Liquide	99.9 mol %
Nitrogen	Air Liquide	99.9 mol %

4.3 Catalyst performance test apparatus

The experimental apparatus consisted of a hydrogen dissolver to completely dissolve the fed hydrogen in the liquid hydrocarbon before reaching the catalyst bed and a fixed bed liquid phase reactor, both mounted in a well-stirred temperature controlled water bath. The flow sheet of the experimental test apparatus is given in figure 4.1. The liquid feed mixture was pumped from the feed bottle via a metering pump. The hydrogen flows were controlled by means of thermal mass flow controllers. A sampling loop was provided downstream of the reactor. Reactor effluent was collected in a product catch pot and effluent gas vented to atmosphere via a needle valve. The major parts of the experimental test apparatus are described in sections 4.3.1 to 4.3.7, all referring to figure 4.1. Valves, fittings, tubing etc. where no specific manufacturer is mentioned, were obtained from Swagelok. All equipment that made contact with the feed and product was made from stainless steel (SS-316).

4.3.1 Improved experimental test apparatus

Following the study undertaken by *Brown (2005)*, a new experimental test apparatus was designed and constructed for this study. There were several modifications compared to the previous setup.

- The previous experimental test apparatus consisted of a single dissolver/reactor stage.
- The new experimental test apparatus was designed so that a second dissolver/reactor stage could be added including the necessary additional upstream facilities.
- Gases from the house gas line were used rather than gases provided by cylinders.
- The stirred oil bath arrangement used by *Brown (2005)* for controlling reaction and dissolver temperature was changed to a stirred water bath. The use of a water bath enabled easier system clean up for catalyst loading and unloading.
- The reactor utilised in the previous experimental test apparatus used by Brown had four fins, protruding 1 cm radially from the reactor body, over the full length. This was designed to break up the vortex formation in the stirred oil bath and to promote heat transfer. Brown though, neither observed a temperature increase in the reactor nor was this an issue at all during this work since the adiabatic temperature rise of the reaction mixture in the hypothetical case of total hydrogen consumption was still < 10 °C (see Appendix B). Therefore, in the new experimental setup the concept of adding fins to the reactors was declined. Indeed, temperature increases were never observed during this work using the re-designed reactors.
- In the previous experimental setup, a top-mounted mechanical stirrer was utilised to ensure vigorous oil flow over the reactor fins. It was decided that this more demanding device was also not necessary and was replaced by a simple magnetic stirrer in the bath.

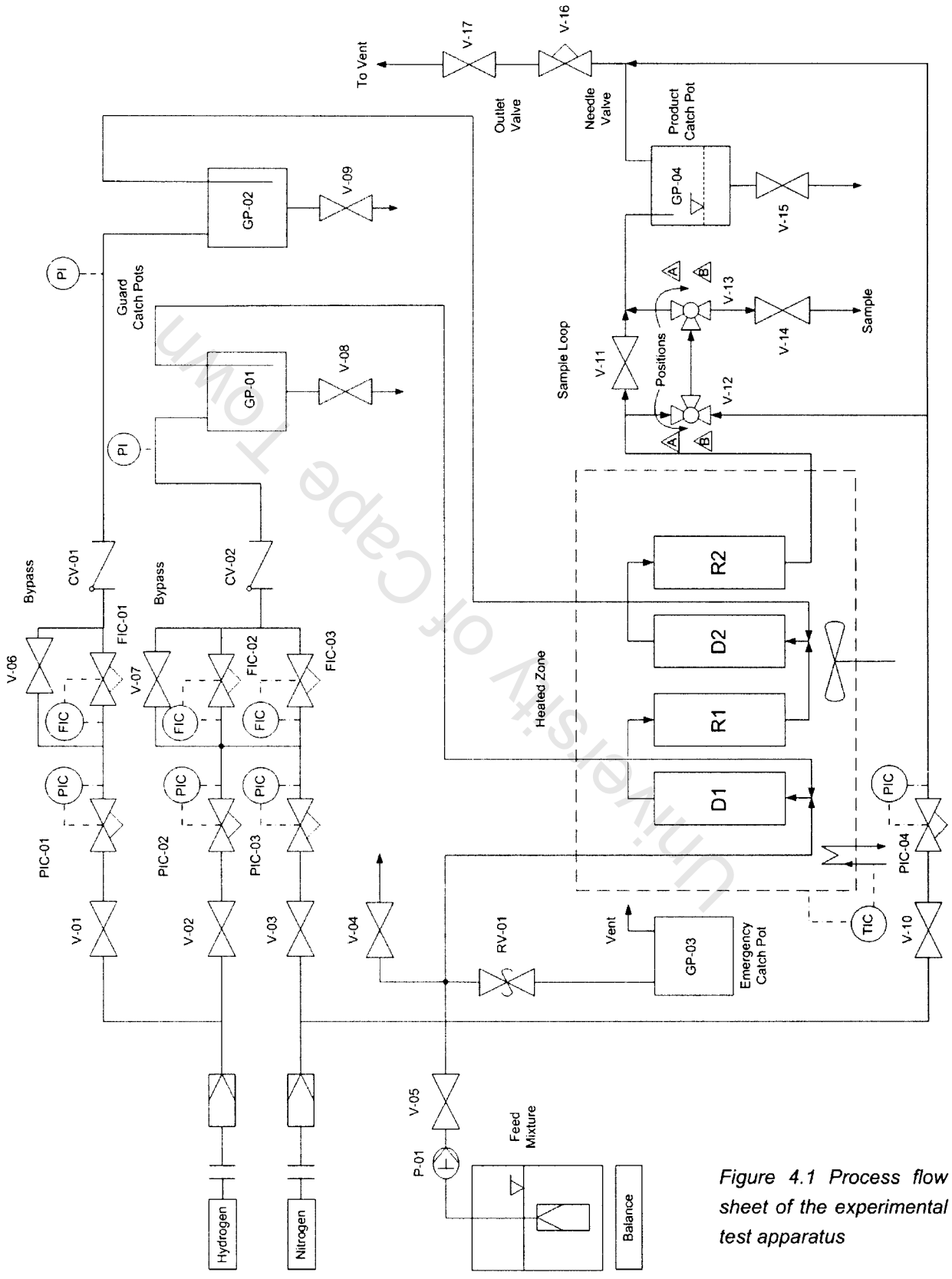

Figure 4.1 Process flow sheet of the experimental test apparatus

4.3.2 Feed system

Hydrogen gas was supplied via the house gas line through valves (V-01 and V-02), and regulated by inline pressure controllers (PIC-01 and PIC-02) (manufactured by Tescom) and thermal mass flow controllers (FIC-01 and FIC-02) (manufactured by UNIT and Brooks, respectively). Check valves (CV-01 and CV-02) and guard catch pots (GP-01 and GP-02) were located downstream of the mass flow controllers. These were designed to provide protection for the mass flow controllers and house gas lines against possible backflow of liquid in case of accidental downstream line or reactor blockage. A metering pump (P-01) (manufactured by HP, HP1100 Series) supplied liquid feed to the dissolver/reactor combination. The range of the pump was 0.001 to 10 ml/min in 0.001 ml/min increments. The feed mixture bottle was placed on a balance (manufactured by Precisa, XB 4200C). This was in order to allow checking of the accuracy of the pump rate and detect possible malfunction. A safety valve (RV-01) was connected to the liquid feed line that would have opened to a catchpot (GP-03) in case of an accidental pressure increase. Over-pressurisation may have led to rupture of equipment, spillage, going off of the hydrogen detectors in the laboratory, automatic switch off of power, damage to the mass flow controllers and damage to the pump.

4.3.3 Hydrogen dissolver

A hydrogen dissolver was installed prior to each reactor. The purpose of this dissolver was to dissolve all fed hydrogen in the liquid feed so that no gaseous hydrogen entered the reactor. The dissolver's body consisted of an 11 cm long stainless steel tube with an internal diameter of 1.6 cm. The dissolver was packed with inert silicon carbide particles (1340 -1660 µm). The dissolver was filled by placing silanised glass wool at the bottom of the dissolver, filling the dissolver with the silicon carbide particles and providing another layer of silanised glass wool at the top. The glass wool prevented the loss of silicon carbide particles from the dissolver. The bottom of the dissolver consisted of an entrance

point for the gas and liquid feeds (¼" Swagelok) whilst the top of the dissolver (¼" Swagelok) was connected to the reactor. The hydrogen was bubbled into the liquid and dissolved. The purpose of the inert silicon carbide particles was to break the hydrogen stream into small bubbles and that way increase the gas/liquid inter-phase area, the radial distribution of the bubbles and the residence time of the hydrogen to enable complete dissolution.

4.3.4 Reactor

A sectional drawing of the reactor is provided in figure 4.2. The reactor body consisted of an 11 cm long stainless steel tube with an internal diameter of 1.6 cm. The top of the reactor comprised a stainless steel gasketed ½" VCR fitting which provided access for loading and unloading of catalyst. The top section included an entrance point for the feed (¼") and an axially centred steel jacketed thermocouple (1/16") (manufactured by Unitemp) whose tip was positioned in the middle of the catalyst bed. The reactor had a bed volume of approximately 22 ml.

4.3.5 Water bath

The dissolvers and reactors were placed in a thermostated bath (manufactured by Neslab) filled with water ("heated zone" in figure 4.1). This ensured isothermal conditions in the dissolvers and reactors. The apparatus maintained the desired temperature by means of a PID controller. Heat was provided by a heating coil submerged in the bath. The bath was continuously stirred using a magnetic stirrer and was covered by an aluminium foil to prevent rapid decline of its level due to evaporation.

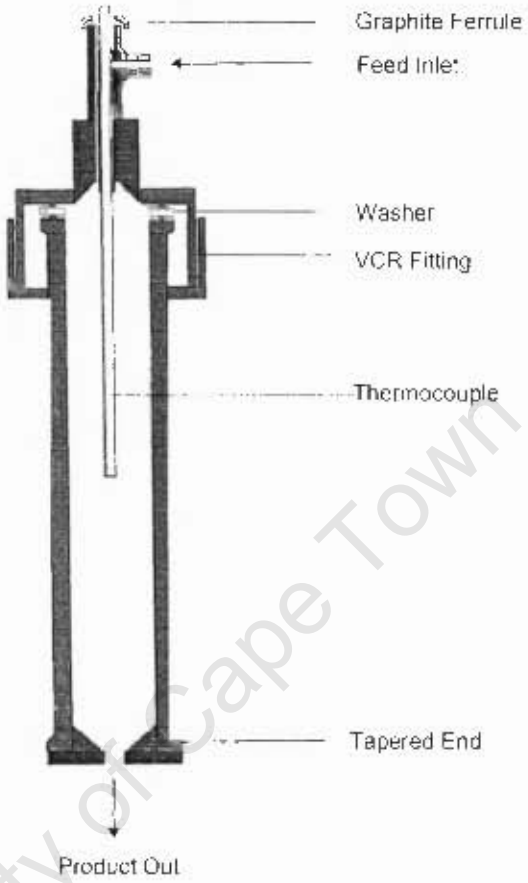

Figure 4.2 Sectional drawing of a reactor

4.3.6 Sampling line

Liquid product samples were collected from the experimental test apparatus and analysed in an off-line gas chromatograph. These samples were collected via the introduction of a sampling loop outside of the water bath containing the dissolvers and reactors. The sampling loop consisted of a 1 ml, 1/8" tube connected to the product line via the two 3-way valves V-12 and V-13 (figure 4.1). The sampling loop could be bypassed via valve V-11. By adjustment of these valves, product flow could be directed through the sample loop or through its bypass. During runs valve V-11 was closed and valves V-12 and V-13 were set on position A to constantly flush the sample loop with the product stream. The sampling line was also connected (via valve V-12) to the line

carrying the pressure regulating nitrogen gas (section 4.3.7) to allow removal of the liquid sample under pressure (via valves V-13 and V-14, then in position B) and to prevent pressure drop when switching the sample loop back in line once the sample had been collected. The instantaneous liquid sample collection method is explained in detail in section 4.4.6. During runs, valve V-11 was closed and valves V-12 and V-13 were set to positions A to constantly flush the sample loop with the product stream.

4.3.7 Pressure control

The pressure in the system was maintained by making use of a pressure regulating gas whose pressure was regulated by an in-line pressure controller (PIC-04). The pressure regulating gas (nitrogen) was added to the gas stream from the reactor downstream of the product catch pot. The combined gas stream was throttled, i.e. it was flow controlled and depressurised, using a regulating needle valve (V-16) before being vented. In this way, the pressure in the reactor was set and maintained constant by the set, constant pressure of the added nitrogen stream.

4.3.8 Auxiliary gases

Nitrogen from the house gas line could also be supplied via valve V-03, regulated via pressure controller PIC-03 and thermal mass flow controller FIC-03 or diverted via the by-pass valve V-07. This nitrogen stream was used for inertising the apparatus, diluting the hydrogen stream for catalyst reduction and flushing the apparatus after the runs.

4.4 Operating procedures for the experimental test apparatus

4.4.1 Catalyst loading

The reactor was packed according to figure 4.3. Note that flow is downwards. A layer of silane treated glass wool was placed at the bottom of the reactor. The purpose of this glass wool was to prevent the loss of packing from the reactor. Above this glass wool, a layer of inert silicon carbide particles (1340 - 1660 μm) was packed. The purpose of this layer of silicon carbide was to provide support for the catalyst bed. Above the layer of silicon carbide, a layer of catalyst particles (see table 4.3 for details of catalyst bed composition) diluted with silicon carbide (1340 - 1660 μm) was added. The purpose of adding the fine grained diluent was to improve hydrodynamic flow patterns in the catalyst bed. The catalyst bed was approximately 5 cm in height and had a volume of 10 cm^3. Above the diluted catalyst bed, another layer of silicon carbide and silanised glass wool was added. The purpose of this layer was to act as a flow distributor. The total volume of the reactor loading was approximately 22 cm^3.

Table 4.3 Composition of catalyst bed (see table 4.1 for properties of catalyst and individual catalyst particles)

Total catalyst mass (g)	1.09±1.5%
Number of catalyst particles	7
Total Pd loading (g)	ca. 0.197
Total Ag loading (g)	ca. 0.142
Total surface area of metal[a] (m^2 / g)	ca. 37

[a] see footnote on table 4.1

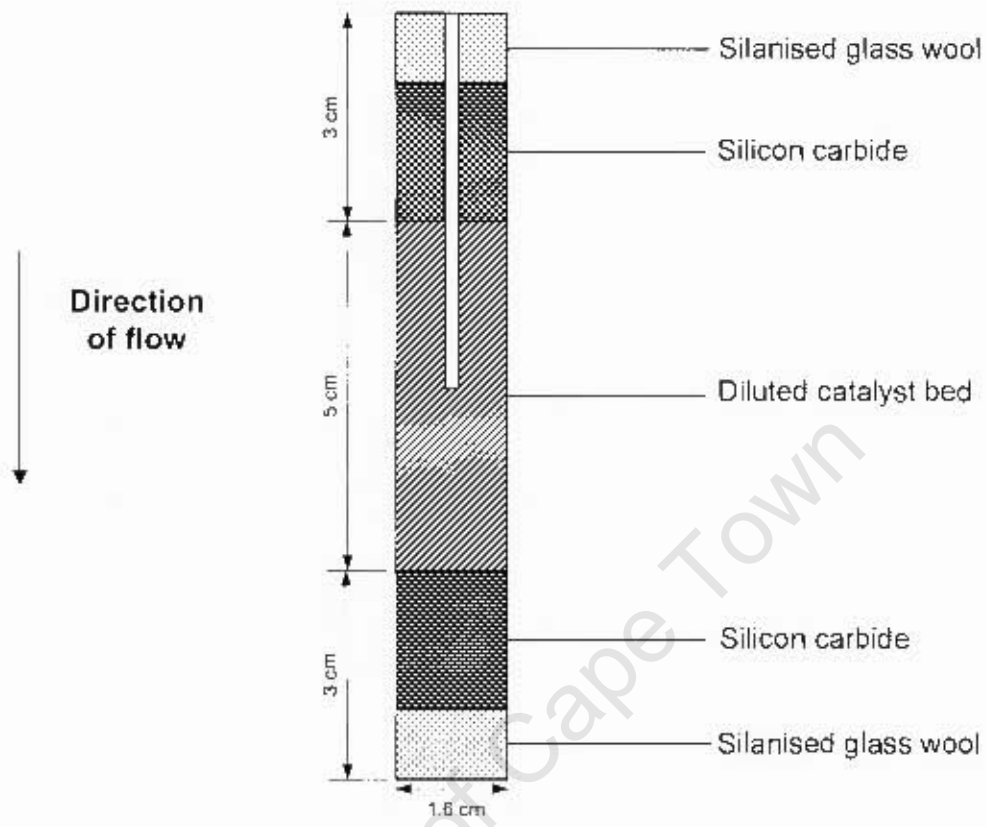

Figure 4.3 Reactor loading

4.4.2 System pressure test

Once the reactor had been packed and mounted, a pressure test on the experimental test apparatus was performed. This was undertaken to ensure that there were no leaks in the system. It was ensured beforehand that the drain valves on the feed and make up hydrogen guard catch pots and the product catch pot (valves V-08, V-09 and V-15) were closed (refer to figure 4.1.). The pressure test was undertaken by closing the outlet valve (V-17) and pressurising the system to 30 bar, using nitrogen via valve V-03, the pressure controller PIC-03 and valve V-07. Then valve V-03 was closed. Large leaks were indicated by an immediate pressure drop and localised via sound and testing thereafter with soapy water solution. These were eliminated by appropriate tightening of the respective fittings and connections. The system was then left under pressure for

a period of several hours. If a pressure drop occurred, each connection was tested using a soapy water solution. Once all leaks had been eliminated and no further pressure drop occurred, the system was flushed of nitrogen and depressurised by opening valve V-17 and after closing valve V-17 again, repressurised to 30 bar using hydrogen via valve V-02, PIC-02 and valve V-07. The leak test was undertaken again. If, after several hours, no pressure drop occurred the apparatus was deemed to be leak tight.

4.4.3 Calibration of mass flow controllers

Prior to the use of the mass flow controllers, it was necessary to calibrate these devices for hydrogen and nitrogen. The mass flow controllers were calibrated by setting the controller to a certain value (as a percentage of its total range) and measuring the real flow via the use of a bubble flow meter. This was undertaken over the entire flow range of the mass flow controllers and calibration graphs were plotted (see appendix D) with the measured flows (at ambient temperature) converted to sccm (standard cubic centimetres per minute) where the standard temperature was 0 °C and the ambient pressure was assumed to be standard pressure of 1 atmosphere.

4.4.4. Catalyst activation / reduction

The heating bath was filled with water and the magnetic stirrer mechanism in the bath was switched on.

The catalyst activation / reduction procedure was performed according to the manufacturer's recommendation, at atmospheric pressure. Valve V-07 was closed and valve V-17 and the throttle valve V-16 were fully opened. A mixture of 5 mol % hydrogen and 95 mol % nitrogen was fed (4 sccm hydrogen and 76 sccm nitrogen) via valves V-02 and V-03 and mass flow controllers FIC-02 and FIC-03. Initially, V-04 was opened for a while to flush back the liquid feed

line and remove any air that might have entered this line while mounting new catalyst. Then valve V-04 was closed. The water bath was heated from ambient temperature at a rate of 1°C / min to a temperature of 90 °C and the reactor was maintained at this temperature for 3 hours. Thereafter, valve V-03 was closed and the flow was changed to hydrogen only via valve V-02 and FIC-02 at 100 sccm. The reactor was maintained at these conditions for a further hour. Thereafter the temperature was set to the intended reaction temperature of 60 °C. Since there was no cooling device applied on the water bath, natural cooling occurred within about an hour. The temperature profile during this procedure is shown graphically in figure 4.4.

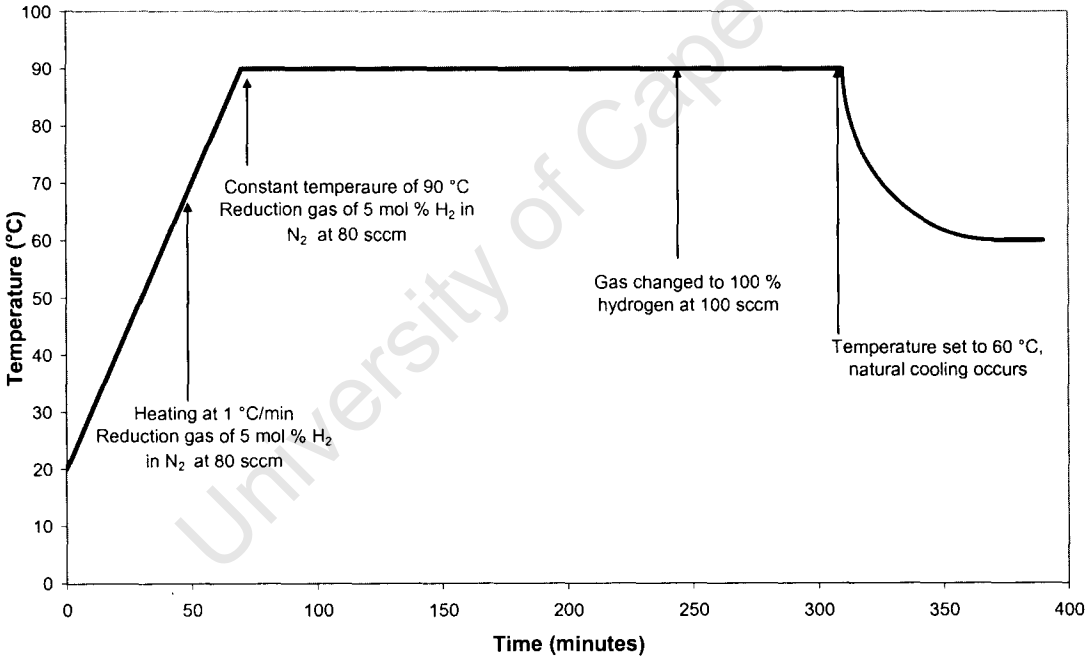

Figure 4.4 Catalyst reduction/activation procedure (at atmospheric pressure)

4.4.5 Start up procedure

Two litres of feed solution were prepared for every run (see appendix C for preparation method of feed mixtures by mass). The temperature controller of the water bath was set to the reaction temperature of 60°C.

For the following refer to figure 4.1. The system was pressurised by closing the outlet valve V-17 and adjusting the hydrogen inlet gas pressure via pressure regulator PIC-02 to 35 bar. The hydrogen pressure was always set 5 bar above the reaction pressure to provide the necessary pressure difference for the functioning of the mass flow controllers. It was ensured that the mass flow controller bypass valve V-07 was open whilst the pressurisation was undertaken. Thereafter valve V-07 was closed and the pressure regulating gas was introduced by opening valve V-10. This was adjusted at 30 bar on pressure controller PIC-04 to obtain the desired reaction pressure. The outlet valve V-17 was opened and the throttle valve V-16 was adjusted to maintain stable flow and system pressure.

It was ensured that both the three-way valves V-12 and V-13 were set to position A, i.e. flow from the reactor through the sample loop to the product catch pot while the sample loop bypass valve V-11 was closed. That way the sample loop was constantly flushed with product. It was also ensured that the liquid sample vent valve V-14 was closed.

Once the system pressure has stabilised, the metering pump (P-01) was primed with the feed mixture to ensure removal of air bubbles trapped in the line from the feed pot to the pump or in the pump head. This was achieved by opening the pump's own purge valve, setting the pump flow rate to 5 ml/min and switching the pump on. Valve V-05 was opened and the purge valve on the pump was closed when no further air bubbles were seen. The procedure was repeated using valve V-04 as the purge valve, which was connected shortly before the inlet to the first dissolver (S1) to ensure that the feed line was bubble free. The apparatus was then primed with feed mixture at this flow rate until liquid could be drawn at the sample valve (see section 4.4.6). Thereafter the required liquid and gas flows were set on the pump and on FIC-02, respectively, and the system was allowed to reach steady state for a period of 24 hours.

4.4.6 Sampling

In order to take a sample, valves V-12 and V-13 were set to position B that allowed flow of nitrogen from the pressure regulating gas line and flow of the sample to the sampling valve, V-14. The sample bypass valve, V-11, was opened. These settings isolated the sampling loop and continued pressurising the sample loop using the pressure regulating gas. A sample vial was placed below the sample valve, V-14. The sample valve was slightly opened and the sample (1 ml) was collected. The vial was closed with an airtight lid, labelled and stored in a refrigerator. Given the high volatility of the product mixture (C_6 hydrocarbons) the small dead volume between valves V-13 and V-14 was blown dry at the end of the sampling procedure by the out-flowing nitrogen stream. Once the sample had been collected, and the line become dry, the sample valve, V-14, was closed. Valves V-12 and V-13 were switched back to product flow from the reactor to the product catch pot (position A). The sample bypass valve, V-11, was closed. This sampling method ensured that no pressure and flow disturbances were introduced into the system and no "old" product contaminated a fresh sample. Samples were taken twice daily.

4.4.7 Draining the product catch pot

The product catch pot (GP-04) had a capacity of 1 litre. It had to be drained regularly to prevent overflow and, effectively, blockage of the outlet lines and liquid flow from the liquid feed line into the gas supply systems. This was accomplished by slightly opening the valve at the bottom of the catch pot, V-15, and collecting the liquid. This was undertaken slowly to prevent depressurisation. Valve V-15 was closed immediately when gas started venting through the drainage line. At a liquid feed flow rate of 0.5 ml/min, the catch pot had to be drained at least every 24 hours. The guard catch pot (GP-01) should not have collected any liquid, but was checked regularly to ensure this was the case.

4.4.8 Alteration of reaction variables

The system pressure was increased by closing the outlet valve, V-17, and using the incoming hydrogen feed stream to pressurise the system. The hydrogen inlet pressure was set on PIC-02 to 5 bar above the desired reaction pressure (to enable FIC-02 working). Once the system pressure had increased to the desired reaction pressure, the pressure regulating gas was set on PIC-04 right to this level. The outlet valve, V-17, was opened to re-establish flow and the throttle valve V-16 re-adjusted. A decrease in the system pressure was achieved correspondingly by first setting the pressure regulating gas back to the desired value (PIC-04) and then decreasing the hydrogen delivery pressure on PIC-02 and opening the throttle valve V-16 a little more to slowly depressurise the system.

The space velocity was altered by adjusting the metering pump (P-01) setting. Proportional to this, the hydrogen flow was also adjusted via FIC-02, to maintain a constant H_2/Oil molar ratio.

A change in the molar H_2/Oil ratio was obtained by only changing the hydrogen flow via FIC-02 at a constant liquid flow rate, i.e. at space velocity still being constant.

After a change in the operating conditions, the system was allowed to re-establish steady state overnight.

4.4.9 Changing the feed bottle

When the currently used feed bottle was almost empty or when a different feed mixture had to be applied, a change of the feed bottle was required. In order to undertake this, the gas flow to the reactor was continued but the pump (P-01) was switched off. Valve V-05 was closed. The current feed bottle was switched

for the fresh one. The pump was primed by opening the pump's own purge valve and setting the pump rate to 5 ml/min. The pump was switched off and the pump's purge valve was closed when no air bubbles were seen in the outflow. The flow rate was then set at the required value, valve V-05 was opened and the pump switched on again. This procedure normally took ca. 5 minutes to undertake.

After a feed bottle change, a period of 8 hours was allowed to elapse as a settling period, before the next sample was taken.

4.4.10 Different series arrangements of dissolvers and reactors

For the various experiments that have been undertaken several different arrangements of hydrogen dissolvers and reactors have been utilised. For these experiments the reactors were loaded with catalyst as described in section 4.4.1 and thereafter connected with ¼" Swagelok fittings in a series arrangement with the dissolvers, as desired. The following arrangements have been set up:

4.4.10.1 Single dissolver and reactor (single stage mode)

This was equal to the experimental setup utilised by *Brown (2005)*. The hydrogen dissolver, D1, was utilised to dissolve all hydrogen in the liquid phase before entering reactor R1. In the corresponding arrangement in this work, hydrogen was added to the dissolver via valve V-02 and via pressure controller PIC-02 and the flowrate controlled via FIC-02.

4.4.10.2 One dissolver and two reactors with no inter-stage hydrogen addition (large reactor mode)

In this setup, one dissolver, D1, was installed with liquid and gas being fed, with the outlet connected to two reactors, R1 and R2, in series. Since both reactors

were packed identically, this arrangement doubled the catalyst mass, in effect doubling the residence time to increase the conversion of the feed (provided the hydrogen in the reaction mixture was not already depleted). Hydrogen was added to the dissolver as in single stage mode via valve V-02 via pressure controller PIC-02 and the flowrate controlled via FIC-02.

4.4.10.3 Two dissolvers and two reactors with inter-stage hydrogen addition (dual stage mode)

In this setup, one dissolver, D1, was installed with liquid and gas feed, with the outlet connected to the first reactor, R1, as in single stage mode. The outflow of this reactor was fed to a second dissolver, D2, where a second stream of hydrogen was added. That way additional hydrogen dissolution was carried out in this second dissolver, D2, and the reaction mixture then passed to a second reactor, R2. This arrangement was expected to yield higher conversions than the previous arrangements, since additional hydrogen was available for reaction. The additional hydrogen could not be added to the first dissolver due to the limited solubility of hydrogen in the feed (see section 2.11, figure 2.21), but only after consumption of the hydrogen (or part of) in reactor R1. Hydrogen addition to the first dissolver, D1, was via valve V-02 via pressure controller PIC-02 and the flowrate controlled via FIC-02 as in previous modes. Hydrogen addition to the second dissolver, D2, was via valve V-01 via pressure controller PIC-01 and the flowrate controlled via FIC-01 (in the single hydrogen dissolver modes described above, valve V-01 was closed).

4.4.11 Checklist for experimental apparatus working properly

During the progress of a run, several routine checks to the test apparatus working properly were regularly undertaken. In these routine checks, the following checklist was performed.

It was ensured that:

- The pump was functioning and the liquid flow rate was at the desired value (derived from the reading of the pump, P-01, and the balance).
- The gas flow rate was at the desired value (FIC-02 reading, and if in dual stage mode, also FIC-01 reading).
- The system pressure was at the desired value (reading on PIC-04) and no pressure drop had occurred.
- The water bath temperature was at the desired value.
- The bath water level had not dropped appreciably; otherwise additional water, preheated to reaction temperature, was added to obtain the desired level.
- The outlet needle valve was sufficiently open and gas flow (pressure control gas) was observed in the bubble meter.
- The amount of feed was sufficient for the run. If this was found to not be the case, the feed bottle was switched for a fresh one in time.
- The product catch pot was drained (via valve V-15).
- The quantity drained from the product catch pot corresponded to the balance reading to confirm the correct quantity pumped.
- The guard catch pot(s) on the hydrogen feed line(s) did not collect liquid (valve(s) V-08 (and V-09)).
- The sample loop valves, V-12 and V-13, the sample valve, V-14, and the bypass valve, V-11, were in the correct positions (positions A and closed, respectively).

4.4.12 Shutdown procedure and catalyst unloading

The feed pump was switched off and valve V-05 was closed. The feed gas was changed from hydrogen to nitrogen, by closing valve V-02 (and valve V-01 if in dual stage mode) and opening valve V-03, at 100 sccm via FIC-03. The system was then allowed to de-pressurise by closing valve V-10, that is switching off the pressure regulating gas and slowly opening the throttle valve, V-16. This was

undertaken to inertise and strip residual hydrocarbons from the system. The sample loop bypass valve (V-11) was also opened. After depressurising, valve V-04 was opened to flush the feed line. After a period of 3 hours, the heating of the water bath was switched off. All remaining liquid was collected from the feed pot, guard catch pots (GP-01 to GP-03) (if there was any) and product catch pot (GP-04). Once the water bath and the reactor had cooled, the water bath was emptied and the reactor was dismounted and opened to change catalyst.

The reactor was mounted in a vice and the top (VCR fitting) was opened with a spanner. The spent catalyst particles were collected and weighed. Thereafter, the spent catalyst and the silicon carbide were discarded. The VCR fitting and thread (see figure 4.2) were cleaned with a brush to remove residual silicon carbide particles. Thereafter the reactor was washed with acetone and dried with compressed air. The reactor was reloaded according to section 4.4.1, a new gasket was inserted into the VCR fitting, the VCR fitting was tightened and the reactor mounted again.

4.4.13 Standby mode

When experimental runs were not being carried out, the experimental test apparatus was switched to standby mode. The heating of the water bath was switched off. Gas supply was switched to nitrogen at 5 sccm in a procedure analogous to shutdown as described in section 4.4.12. The liquid flow rate was set to 0.01 ml/min, whilst the pressure regulating gas was maintained at 30 bar. This was undertaken in order to prevent catalyst deactivation and coking. The throttle valve, V-16, was opened just slightly to ensure flow. Valves V-12 and V-13 were set to position A. The sample loop bypass valve, V-11, the sampling valve, V-14, and the product catch pot drainage valve, V-15, were closed.

The procedure for return from standby mode to operation was analogous to the start-up procedure (section 4.4.5).

4.4.14 Emergency shutdown procedure

Due to the sensitive nature of laboratory equipment, it was important that safety precautions be implemented to protect co-workers and the laboratory environment and to prevent damage to expensive equipment. The following steps had to be undertaken in the event of an emergency shutdown being required:

- Switch off the main power supply. This stops the pumps, closes the mass flow controllers and stops the heating of the water bath.
- Switch off all working gas supply lines (valves V-02 and V-10, also V-01 if in dual mode).

Once the emergency situation was over, nitrogen supply should have been switched on (either via opening valve V-03 and switching on FIC-03 or via valve V-03 and the FIC by pass valve V-07) and all hydrocarbons should be flushed out of the apparatus, without repressurising or reheating, analogous to the regular shut-down procedure (see section 4.4.12) but flushing longer.

4.4.15 The hydrogen dissolution experiments

The purpose of the hydrogen dissolution experiments was to test whether or not under the operating conditions, the hydrogen fed to the dissolver achieved complete dissolution in the liquid phase when leaving the dissolver and before entering the reactor and whether complete dissolution was achievable or not using the available equipment, i.e. the silicon carbide loaded dissolver described in section 4.3.3. Complete dissolution can only take place within the thermodynamically defined window (section 2.11, figure 2.21) which is a function of temperature (the experiment was carried out at 60°C), H_2/Oil molar ratio and total pressure. However, this may be superimposed by kinetic limitations in the dissolver, in particular the liquid flow rate and design parameters that determine

residence times and extent of gas dispersion and thus may narrow the operation window.

A test method was devised to determine the real operation window of the given dissolver. A T-shaped pipe connection replacing the elbow that leads to the reactor and is there for normal operation, was installed vertically at the top of the hydrogen dissolver followed by a short ¼" line of ca. 5 ml internal volume with a ¼ " valve and a clear hose tube on top (see figure 4.5).

For a particular H_2/Oil molar ratio, a certain pressure and 60°C dissolver temperature, a liquid flow rate of the pump was set and this feed allowed to flow through the dissolver apparatus (and then out through the reactor feed line into the pressure regulation system). The operation was allowed to equilibrate for a period of two hours.

During this period, if the hydrogen was completely dissolved in the liquid, the volume of the top ¼" tube filled with liquid. However, if undissolved hydrogen was present, it would have collected in this volume in gaseous form. In order to check this, valve V-18, at the top of the dissolver, was opened and the line was sampled through the transparent hose tube for the presence of gaseous hydrogen. If gas flow was observed immediately after this valve was opened, the hydrogen was deemed not to have completely dissolved in the oil since it was the remaining bubbles of undissolved hydrogen that collected on top of the liquid and with time filled the ¼" tube. On the other hand, if a stream of foaming liquid appeared immediately, then the hydrogen was deemed to have completely dissolved in the oil, meaning that a gas loaded liquid was collected in the ¼" tube that separated only – but – immediately when depressurised (through opening the valve, V-18), analogous to opening a bottle of champagne. This procedure was undertaken for the applied reaction temperature of 60 °C and an array of pressures of 15, 30 and 60 bar, molar H_2/Oil ratios of 0.005, 0.01, 0.015 and

0.03, i.e. 0.5, 1.0, 1.5 and 3.0 mol% hydrogen and liquid flow rates from 0.5 to 4 ml/min.

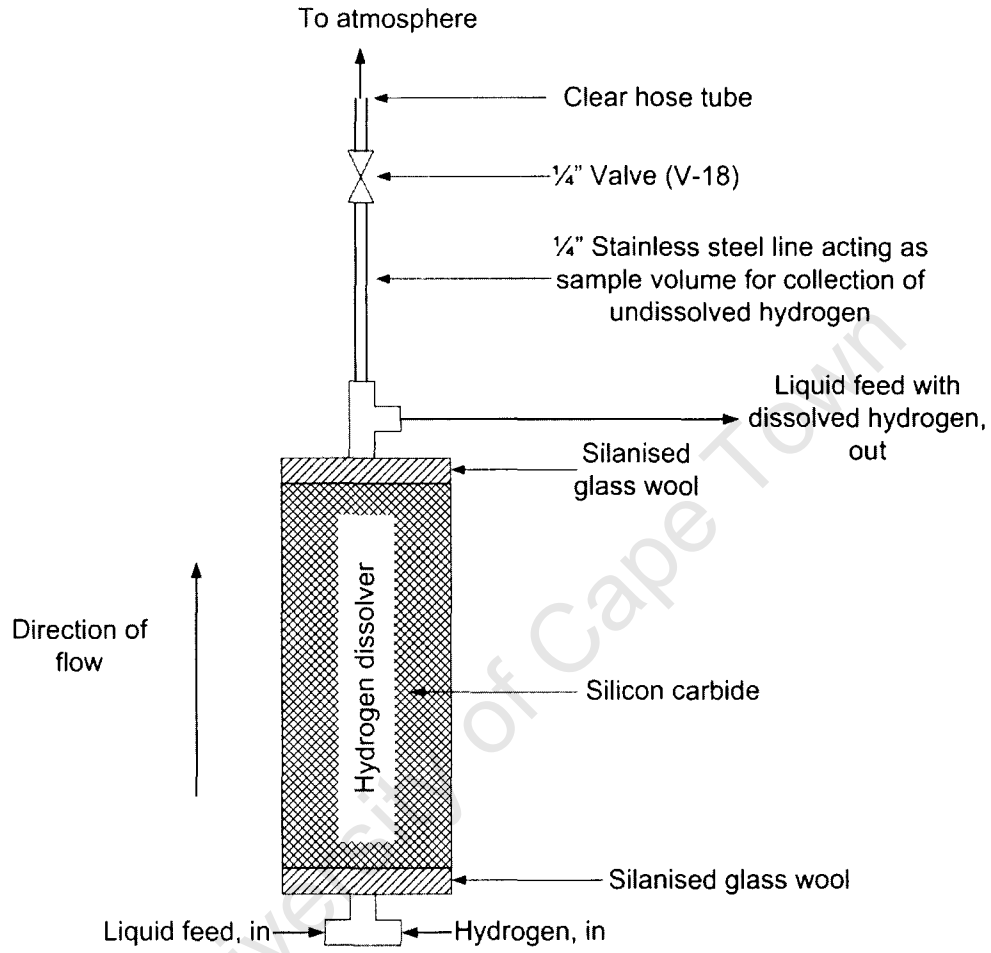

Figure 4.5 Sectional drawing of a hydrogen dissolver with additional device on top utilised for hydrogen dissolution experiments

4.5 Sample analysis

4.5.1 Gas chromatography

Feed and product liquid sample analyses were undertaken using gas chromatography with flame ionisation detection. A different column was utilised for this study, compared to the study undertaken by *Brown (2005)*. The previous column was a fused silica capillary column with a rather unpolar dimethylpolysiloxane stationary phase (PONA) that separated essentially according to boiling points. The new column was a fused silica capillary column with an Al_2O_3/Na_2SO_4 stationery phase. This column was polar and, therefore, facilitated better separation, namely groupwise separation, of the saturated, unsaturated and highly unsaturated compounds utilising the different polarisabilities of single, double and triple bonds. Samples were injected manually. Details of the gas chromatographic equipment are given in table 4.4.

Details of the temperature programs applied, sample preparation, volumes injected etc. are given in table 4.5.

Peak identification was undertaken by use of pure model compounds. A full analysis of all the compounds present was not undertaken, as the unidentified peaks ('unknowns') were essentially introduced with the 1-hexene feed component and amounted to less than 0.5 % of the total feed and product. They have been found to be essentially inert under operational conditions applied compared to the added impurity. The peaks of interest were that of 1-hexyne (the added model impurity), 1-hexene and n-hexane (the full hydrogenation product) which have been identified making up more than 99.5 % of the total peak area of the product chromatograms. Peaks in the region expected for cracking or hydrogenolysis products ($< C_6$) were not observed. Also, dimers (in the C_{12} range) were not observed.

Table 4.4 Specifications of the gas chromatographic equipment and method

Gas chromatograph	Varian model 3700
Detector	Flame ionisation detector
Carrier gas	Hydrogen
Make-up gas	Hydrogen
Column head pressure	1.75 bara
Injector temperature	200 °C
Detector temperature	270 °C
Column type	PLOT fused silica column
Stationary phase	Al_2O_3/Na_2SO_4
Manufacturer	Chrompack
Catalogue no.	CP7568
Column length	50 m
Column internal diameter	0.53 mm
Column maximum temperature	200 °C

4.5.2 FID analysis

FID response factors for all components were considered to be unity with respect to carbon mass. This was justified on the basis of the signal of hydrocarbons in the flame ionisation detector being proportional to the amount of carbon, so that the molar response of any of the C_6 hydrocarbons present in the feed or product was equal. Since no peaks of other carbon number hydrocarbons or hetero-compounds were present, peak area percentage was identical with molar percentage and peak areas proportional to moles.

Brown's (2005) analyses and also the initial sample analyses within this work were based on the assumption that all peaks were correctly integrated. But it became clear soon that this assumption was wrong and peak integration was not

accurate enough under the given circumstances. The reason for this was the large difference in relative percentages and thus peak areas of the compounds being analysed. The 1-hexene peak constituted 98+ % of the total peak area whilst the remaining compounds of interest were present in percentages of less to far less than one. Despite the wide linear range of the flame ionisation detector, it was impossible to analyse for the huge 1-hexene peak and the tiny 1-hexyne and n-hexane peaks simultaneously in a single GC analysis. It was observed that when peaks of the trace compounds were large enough to accurately determine peak areas, conversions and selectivities, the 1-hexene peak obtained was several minutes wide, neither Gaussian nor at least smoothly shaped and apparently highly overloaded with respect to both the GC column and the linear range of the FID. When attempts were made to decrease the sample size and/or increase the split ratio to decrease this peak's size, the smaller peaks were too small to be accurately integrated or even detected. Due to the large peak area of the 1-hexene peak, inaccuracies in the determination of this peak area would greatly affect all mole fractions calculated. Indeed, the results obtained by this method were neither accurate nor repeatable. As such a new analysis technique was required. This is demonstrated in figure 4.6 which has been reproduced from *Brown (2004)* and figure 4.7 which was obtained from the preliminary results of this work.

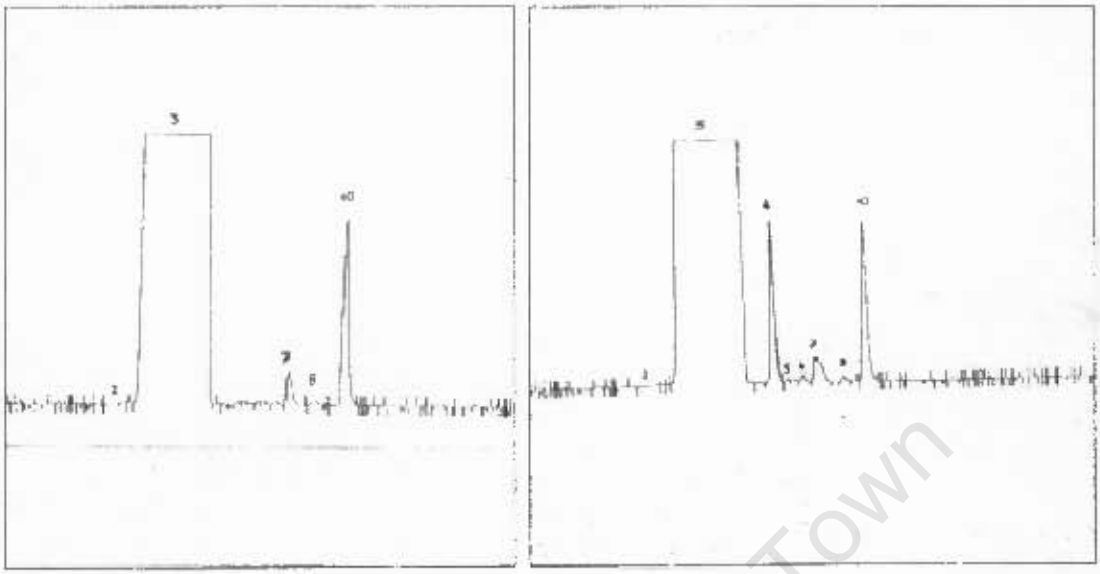

Figure 4.6 Sample GC trace (from PONA column) taken from Brown (2004, pp. 74)

(Experiment 9: 1 mol% 1-hexyne in 1-hexene; P = 15 bar; T = 60°C)

left: feed

right: product

Peak number	Time (minutes)	Compound
2	10.59	3-methyl-pentane
3	11.31	1-hexene
4	12.00	n-hexane
5	12.12	3-hexene (trans and cis)
6	12.28	(trans) 2-hexene
7	12.47	2-methyl-2-pentene
8	12.82	unknown
10	13.77	1-hexyne

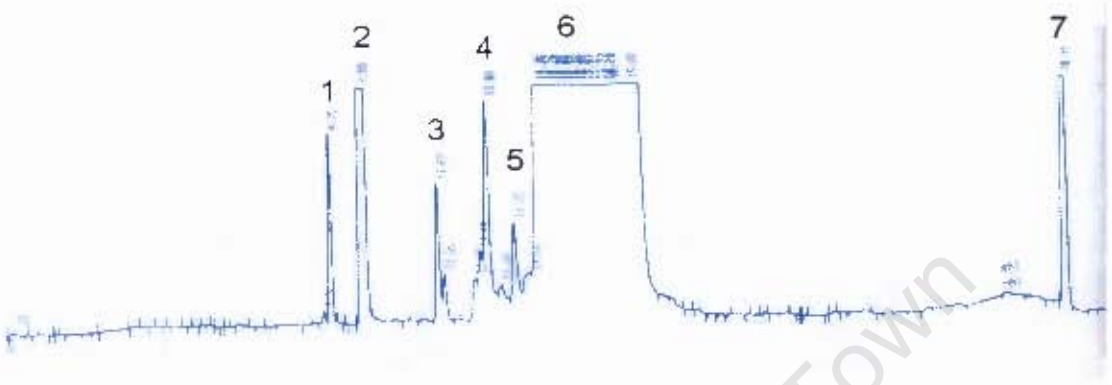

Figure 4.7 Sample GC trace (from Al_2O_3/Na_2SO_4 column) (Experiment 1: Table 5.2)

Peak number	Time (minutes)	Compound
1	8.75	unknown
2	9.55	n-hexane
3	11.67	unknown
4	13.01	unknown
5	13.73	unknown
6	14.30-16.81	1-hexene
7	28.45	1-hexyne

4.5.3 Internal standard method

It was decided to carry out two analyses per sample, the one with a small, the other with a large volume injected, supported by high and low split ratio, respectively, in order to get accurate results from each of these analyses for the integration of the large peaks and the small peaks. The two chromatograms were brought together by means of an internal standard mixture. The internal standard mixture was added to each sample prior to the two different injections into the gas chromatograph.

Criteria for the selection of the constituents of the internal standard mixture were the following:

- Must be hydrocarbons so that the carbon specific FID response factor was still unity as for the other compounds.
- Must be well separable by the GC column from the other compounds present in the sample.
- Must be C_6 compounds in order to be detected in the same retention time range as the other compounds present in the sample.
- Must be C_6 compounds in order to have volatilities similar to the other constituents of the sample to avoid discrimination in the injector.
- Must be readily available.
- Must be relatively cheap since relatively large quantities were required.

Consequently, a mixture of ca. 2 wt. % 2-methyl pentane in cyclohexane was prepared and added in a ca. 1:1 volume ratio to each sample. Note that the ratio of the two constituents of the internal standard mixture had to be 50:1 only in approximation but the value itself had to be determined as accurate as possible (by weighing in on high precision balances). The method of preparing this mixture is analogous to the preparation of the reaction feed mixture by mass, which is presented in Appendix C. Correspondingly, the amount added to the feed and product samples for GC analysis needed to result in an approximately 1:1 ratio only. Each sample was analysed twice under conditions optimised for accurately measuring either the small or large peaks. The 2-methyl pentane peak was utilised as the reference for the small n-hexane and 1-hexyne peaks whilst the cyclohexane peak was used as the reference for the large 1-hexene peak. The GC conditions for the analyses with the internal standard mixture are given in table 4.5.

Table 4.5 GC conditions for analyses using the internal standard mixture

	Analysis 1 – small peaks	Analysis 2 - large peaks
Split ratio	Low, 1:1	High, 100:1
Injected volume	High, 0.3 µl	Low, 0.05 µl
Temperature program	80 °C for 2 min. 3 °C / min to 130 °C (until n-hexane peak was observed). 10 °C / min to 200 °C. 200 °C until stopped manually.	Isothermal at 160 °C, until stopped manually.

Figures 4.8 and 4.9 show examples of the typical chromatograms obtained.

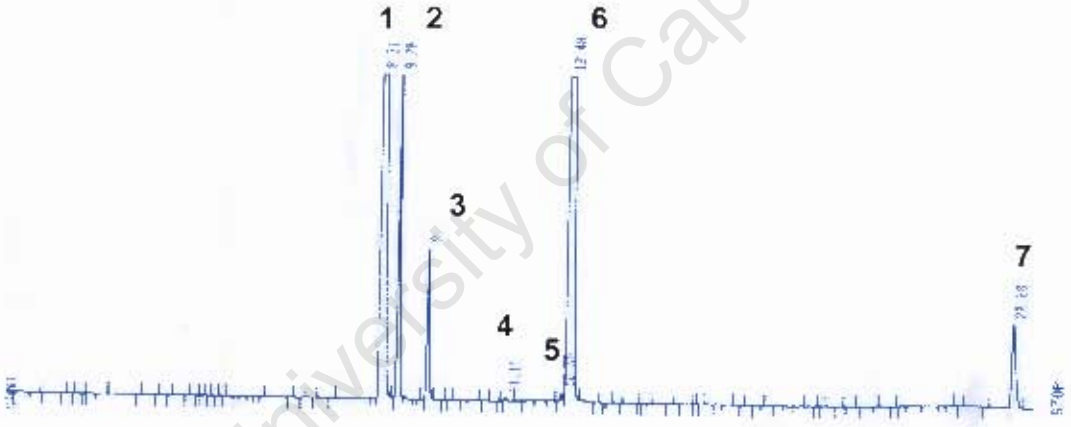

Figure 4.8 Sample GC trace using internal standard method, high injection volume/low split analysis (Experiment 1: Table 5.2)

Peak number	Time (minutes)	Compound
1	8.31	cyclohexane
2	8.70	2-methyl pentane
3	9.37	n-hexane
4	11.11	unknown
5	12.35	unknown
6	12.48	1-hexene
7	22.28	1-hexyne

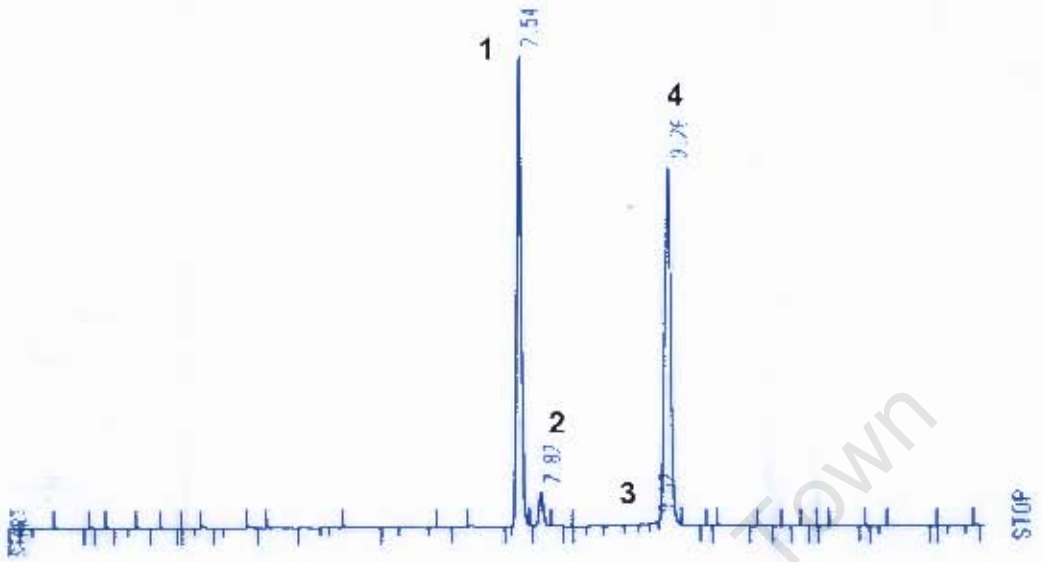

Figure 4.9 Sample GC trace using internal standard method, low injection volume/high split analysis (Experiment 1: Table 5.2)

Peak number	Time (minutes)	Compound
1	7.54	cyclohexane
2	7.87	2-methyl pentane
3	9.57	unknown
4	9.76	1-hexene

An amount of internal standard mixture was added to each sample, be it feed or product that resulted in an approximately 1:1 volume ratio of sample and internal standard. From the two GC analyses performed, the peaks and designations of the respective peak areas that were obtained are given in table 4.6.

Table 4.6 Compounds observed in GC analyses and designations of peak areas

High injection volume/low split GC analysis		Low injection volume/high split GC analysis	
Compound	**Peak area**	**Compound**	**Peak area**
1-Hexyne	A_1	1-Hexene	A_4
n-Hexane	A_2	Cyclohexane (internal standard)	S_2
2-Methyl pentane (internal standard)	S_1		
Unknowns	A_3		

4.5.4 Catalyst/process performance evaluation parameters – Determination of conversions and selectivities using the internal GC standard method

4.5.4.1 Accuracy of the internal standard method

In table 4.6, the molar compositions are compiled for some examples of the different charges of feed mixture prepared as weighed in (see description of method in Appendix C) and as analysed by the internal standard gas chromatographic method, according to the following calculations:

The molar ratio of the impurity to 1-hexene in the feed mixture is as follows (indices as defined in table 4.6):

$$\left(\frac{n_1}{n_4}\right)_{feed} = \left(\frac{A_1}{A_4}\right)_{feed} \quad (1)$$

Extended by $\left(\frac{S_1}{S_2}\right)\left(\frac{S_2}{S_1}\right)$:

$$\left(\frac{n_1}{n_4}\right)_{feed} = \left(\frac{A_1}{A_4}\right)_{feed}\left(\frac{S_1}{S_2}\right)\left(\frac{S_2}{S_1}\right) \quad (2)$$

$$\left(\frac{n_1}{n_4}\right)_{feed} = \left(\frac{A_1}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}\left(\frac{S_1}{S_2}\right) \quad (3)$$

where $\left(\frac{A_1}{S_1}\right)$ was obtained from the high injection volume/low split GC analysis (small peaks)

$\left(\frac{S_2}{A_4}\right)$ was obtained from the low injection volume/high split GC analysis (large peaks)

and $\left(\frac{S_1}{S_2}\right)$ represents the ratio of the two components as accurately weighed into the internal standard mixture

Then the molar impurity content in the feed is:

$$x_{impurity,feed} = \frac{\left(\frac{n_1}{n_4}\right)_{feed}}{\left(\frac{n_1}{n_4}\right)_{feed} + 1} \quad (4)$$

$$x_{impurity,feed} = \frac{\left(\frac{A_1}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}\left(\frac{S_1}{S_2}\right)}{\left(\frac{A_1}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}\left(\frac{S_1}{S_2}\right) + 1} \quad (5)$$

This equation ignores that a small amount of unknown compounds were present in the mixture. However, these 'unknowns' where brought in with the 1-hexene, were found to be inert under reaction conditions and added up to less than

0.5 mol % of the total feed and product (section 4.5.1). Therefore, these unknowns could be neglected calculating $n_{1-hexyne}/n_{1-hexene}$ of the feed.

The high injection volume/low split analysis that was utilised to obtain the peak area of 1-hexyne was undertaken once per each sample. The low injection volume/high split analysis was utilised to obtain the peak area of 1-hexene (which made up approximately 99 mol% of the feed). Therefore it was necessary to undertake this analysis twice. The molar composition for each sample was calculated twice utilising the two low injection volume/high split analyses, and the results averaged to obtain the molar composition for that sample (table 4.7).

Results given in table 4.7 for the contents of 1-hexyne weighed in and analysed give proof that the newly developed internal standard gas chromatography method is correct and accurate.

The evaluation of GC analyses of product samples (sections 4.5.4.2 to 4.5.4.7) was based on the analysed data.

Table 4.7 Comparison of the molar compositions of some examples of the different charges of feed mixture prepared as obtained from weighing in (as described in Appendix C) and from the gas chromatographic analysis with the newly developed internal standard method

a. Molar composition calculated as per accurate weighing in (examples)

Feed for run no.	Weighed in quantity				Content of 1-hexyne weighed in (mol %)
	1-hexyne mass (g)	1-hexyne (moles)	1-hexene mass (g)	1-hexene (moles)	
1	17.783	0.216	1752.147	20.819	**1.029**
2	16.759	0.204	1680.367	19.966	**1.011**
3	13.679	0.167	1461.981	17.371	**0.950**

b. Molar composition calculated as per internal standard method (examples)

Feed for run no.	Peak areas					Standard mixture - molar ratio[a] (S_1/S_2)	Content of 1-hexyne analysed (mol %)	Content of 1-hexyne analysed average (mol %)
	1-hexene (A_4)	cyclohexane (S_2)	1-hexyne (A_1)	n-hexane (A_2)	2-methyl pentane (S_1)			
1	427890	354330	36187	7891	58318	0.02022	1.026	**1.027**
	266100	220950					1.029	
2	293890	259620	26260	4437	45466	0.02022	1.019	**1.016**
	227540	199740					1.013	
3	43302	46211	15331	3700	34450	0.02022	0.949	**0.944**
	43276	45735					0.940	

[a] A volume of standard mixture was prepared that was sufficient to last for analysing all samples gained

4.5.4.2 Conversion of impurity (1-hexyne)

The calculation of impurity conversion considered only impurity hydrogenation, since isomerisation of the triple bond or skeletal isomerisation of the impurity was not considered to be a net removal of impurity (however, no isomerisation was observed). The conversion of the impurity was defined as follows:

$$X_{impurity} = \frac{x_{impurity,feed} - x_{impurity,product}}{x_{impurity,feed}} \tag{6}$$

$$X_{impurity} = \frac{\left(\frac{A_1}{\sum A_i}\right)_{feed} - \left(\frac{A_1}{\sum A_i}\right)_{product}}{\left(\frac{A_1}{\sum A_i}\right)_{feed}} \tag{7}$$

where $\sum A_i = A_1 + A_2 + A_3 + A_4$

Equation (2) extended by $\left(\frac{S_2}{S_1}\right) \Big/ \left(\frac{S_2}{S_1}\right)$ and $\left(\frac{A_4}{A_4}\right)$:

$$X_{impurity} = \frac{\left[\frac{\left(\frac{A_1}{\sum A_i}\right)_{feed}\left(\frac{S_2}{S_1}\right)\left(\frac{A_4}{A_4}\right)}{\left(\frac{S_2}{S_1}\right)}\right] - \left[\frac{\left(\frac{A_1}{\sum A_i}\right)_{product}\left(\frac{S_2}{S_1}\right)\left(\frac{A_4}{A_4}\right)}{\left(\frac{S_2}{S_1}\right)}\right]}{\left[\frac{\left(\frac{A_1}{\sum A_i}\right)_{feed}\left(\frac{S_2}{S_1}\right)\left(\frac{A_4}{A_4}\right)}{\left(\frac{S_2}{S_1}\right)}\right]} \tag{8}$$

rearranged:

$$X_{impurity} = \frac{\left[\frac{\left(\frac{A_1}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}\left(\frac{A_4}{\sum A_i}\right)_{feed}}{\left(\frac{S_2}{S_1}\right)}\right] - \left[\frac{\left(\frac{A_1}{S_1}\right)_{product}\left(\frac{S_2}{A_4}\right)_{product}\left(\frac{A_4}{\sum A_i}\right)_{product}}{\left(\frac{S_2}{S_1}\right)}\right]}{\left[\frac{\left(\frac{A_1}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}\left(\frac{A_4}{\sum A_i}\right)_{feed}}{\left(\frac{S_2}{S_1}\right)}\right]} \quad (9)$$

where $\left(\frac{A_1}{S_1}\right)$ was obtained from the high injection volume/low split GC analysis (small peaks)

$\left(\frac{S_2}{A_4}\right)$ was obtained from the low injection volume/high split GC analysis (large peaks)

$\left(\frac{A_4}{\sum A_i}\right)$ was obtained from the low injection volume/high split GC analysis (large peaks)

and $\left(\frac{S_2}{S_1}\right)$ represents the ratio of the two components as accurately weighed into the internal standard mixture

4.5.4.3 Conversion of 1-hexene

The conversion of 1-hexene was simply the difference of the 1-hexene contents in the feed and product streams. The loss of 1-hexene to whatever, be it via hydrogenation (to n-hexane), via isomerisation (to i-hexenes) or else, was the basis of this equation. Conversion of impurity to 1-hexene may have resulted in a negative conversion of 1-hexene, in other words a net gain in 1-hexene, which would have been desirable. The conversion of 1-hexene was defined as follows:

$$X_{1-hexene} = \frac{x_{1-hexene,feed} - x_{1-hexene,product}}{x_{1-hexene,feed}} \tag{10}$$

$$X_{1-hexene} = \frac{\left(\frac{A_4}{\sum A_i}\right)_{feed} - \left(\frac{A_4}{\sum A_i}\right)_{product}}{\left(\frac{A_4}{\sum A_i}\right)_{feed}} \tag{11}$$

And the final equation was developed, analogous to developing the equation for impurity conversion:

$$X_{1-hexene} = \frac{\left[\frac{\left(\frac{A_4}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}\left(\frac{A_4}{\sum A_i}\right)_{feed}}{\left(\frac{S_2}{S_1}\right)}\right] - \left[\frac{\left(\frac{A_4}{S_1}\right)_{product}\left(\frac{S_2}{A_4}\right)_{product}\left(\frac{A_4}{\sum A_i}\right)_{product}}{\left(\frac{S_2}{S_1}\right)}\right]}{\left[\frac{\left(\frac{A_4}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}\left(\frac{A_4}{\sum A_i}\right)_{feed}}{\left(\frac{S_2}{S_1}\right)}\right]} \tag{12}$$

4.5.4.4 Specificity

Specificity was defined by *McPherson (2003)* as the overall reaction 'selectivity' in respect of desired (impurity removed) and undesired (1-hexene loss) reactions and is defined as follows

$$Sp = \frac{X_{impurity+impurity\ isomers}}{X_{1-hexene}} \quad (13)$$

Where $X_{impurity+impurity\ isomers}$ was to equal to the removal of the impurity (1-hexyne) and all its possibly forming isomers (however, no impurity isomerisation was observed in this study)

and $X_{1-hexene}$ was to equal to the loss of 1-hexene, regardless whether by hydrogenation or double bond isomerisation (however, no double bond isomerisation was observed in this study).

A high specificity indicated that the extent of impurity removal compared favourably to the loss of 1-hexene.

In order to determine the average specificty of a number of data points in a specificity plot (for instance figure 5.7), a trend line through these data points and the origin was determined, whose slope gave the specificity.

4.5.4.5 Selectivity

4.5.4.5.1 Selectivity of 1-hexyne conversion

1-Hexyne can react to either 1-hexene or n-hexane but that cannot be distinguished in this system, anyway. However, 1-hexyne could also react to its internal triple bond isomers (as illustrated in figure 2.4) or skeletal isomers or an

alkadiene. However, since no such isomers were observed, selectivity of 1-hexyne conversion was always 100 %.

4.5.4.5.2 Hydrogenation selectivity

Selectivity of hydrogenation was defined by *McPherson (2003)* as the ratio of conversion of impurity and 1-hexene via hydrogenation to the conversion of impurity and 1-hexene via hydrogenation and isomerisation. Since neither isomerisation of the 1-hexene nor isomerisation of the 1-hexyne was observed, hydrogenation selectivity was always 100%.

4.5.4.6 Hydrogen consumption

Hydrogen consumption resulted from 1-hexene and impurity hydrogenation. 1-Hexyne could have been hydrogenated to an alkene and subsequently (or not) to n-hexane. Therefore, net hydrogen consumption could be determined by just considering impurity conversion and n-hexane formation

$$H_2\ consumption\ [mol_{H_2} / mol_{feed}] = (x_{n-hexane,product} - x_{n-hexane,feed}) + (x_{impurity,feed} - x_{impurtiy,product}) \quad (14)$$

It follows, analogous to developing the equation for impurity conversion:

$$H_2\ consumption\ [mol_{H_2}/mol_{feed}] =$$

$$\left[\left(\frac{\left(\frac{A_4}{\sum A_i}\right)_{product}\left(\frac{A_2}{S_1}\right)_{product}\left(\frac{S_2}{A_4}\right)_{product}}{\left(\frac{S_2}{S_1}\right)}\right)-\left(\frac{\left(\frac{A_4}{\sum A_i}\right)_{feed}\left(\frac{A_2}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}}{\left(\frac{S_2}{S_1}\right)}\right)\right]+ \quad (15)$$

$$\left[\left(\frac{\left(\frac{A_4}{\sum A_i}\right)_{feed}\left(\frac{A_1}{S_1}\right)_{feed}\left(\frac{S_2}{A_4}\right)_{feed}}{\left(\frac{S_2}{S_1}\right)}\right)-\left(\frac{\left(\frac{A_4}{\sum A_i}\right)_{product}\left(\frac{A_1}{S_1}\right)_{product}\left(\frac{S_2}{A_4}\right)_{product}}{\left(\frac{S_2}{S_1}\right)}\right)\right]$$

Hydrogen conversion was then calculated by dividing hydrogen consumption by the molar H_2/Oil ratio, where "Oil" refers to the total liquid feed of 1-hexene and impurity.

$$X_{H_2} = \frac{H_2\ consumption\ [mol_{H_2}/mol_{feed}]}{\left(\frac{H_2}{Oil}\right)_{molar,feed}} \quad (16)$$

It was found previously *(Brown, 2004)* that the impurity, once reacting, was instantaneously saturated to n-hexane over this catalyst with only traces of possible 1-hexene intermediate desorbing from the catalyst particles. This means that for each mole of impurity consumed, two moles of hydrogen are consumed. However, this does not affect the value of X_{H_2} and was not a boundary condition for the equations.

5 RESULTS

5.1 Hydrogen dissolution runs

The hydrogen dissolution runs were a crucial part of this study. The purpose of the hydrogen dissolution runs was to test whether under the operating conditions the hydrogen fed to the hydrogen dissolver achieved complete dissolution in the liquid phase before leaving the dissolver and entering the reactor and whether or not complete dissolution was achievable using the silicon carbide loaded hydrogen dissolver described in section 4.3.3. The experimental setup and method for these runs and the sampling technique were fully described in section 4.4.15. Table 5.1 illustrates the array of conditions at which the hydrogen dissolution runs were undertaken.

Table 5.1 Conditions at which hydrogen dissolution runs were undertaken

Temperature (°C)	H_2/Oil molar ratio	Pressure (bar)	Pump rate (ml/min)
60[a]	0.005	15, 30, 60	0.10 – 4.0
60[a]	0.010	15, 30, 60	0.05 – 3.2
60[a]	0.015	15, 30, 60	0.05 – 3.0
60[a]	0.030	15, 30, 60	0.05 – 1.2

[a] Applied reaction temperature in all of the selective hydrogenation experiments (see table 5.2)

Figures 5.1 to 5.4 illustrate the determination of the region where the hydrogen fed to the dissolver was deemed to be or not to be completely dissolved in the liquid phase at the set pressures. The minimum pressure required for complete dissolution of the fed hydrogen in the liquid ('Oil') phase (thermodynamic limit) was determined from figure 2.21.

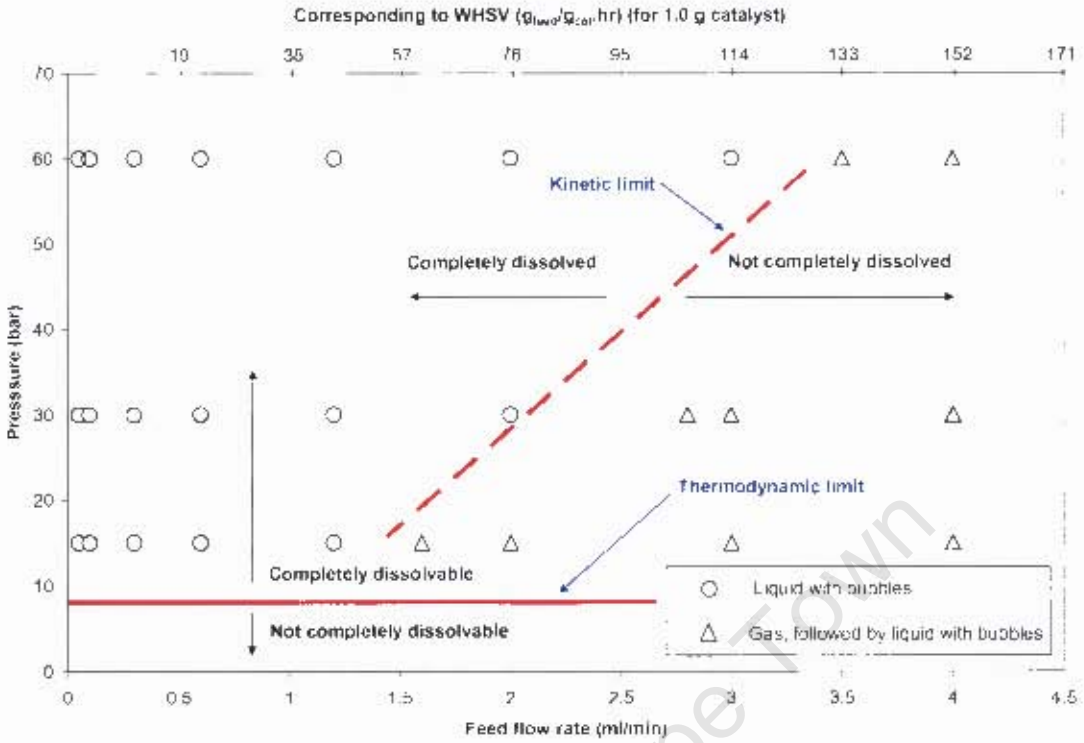

Figure 5.1 Solubility of hydrogen in 1-hexene as a function of pressure (bar) and feed flow rate (ml/min) at H_2/Oil molar ratio = 0.005 and 60 °C

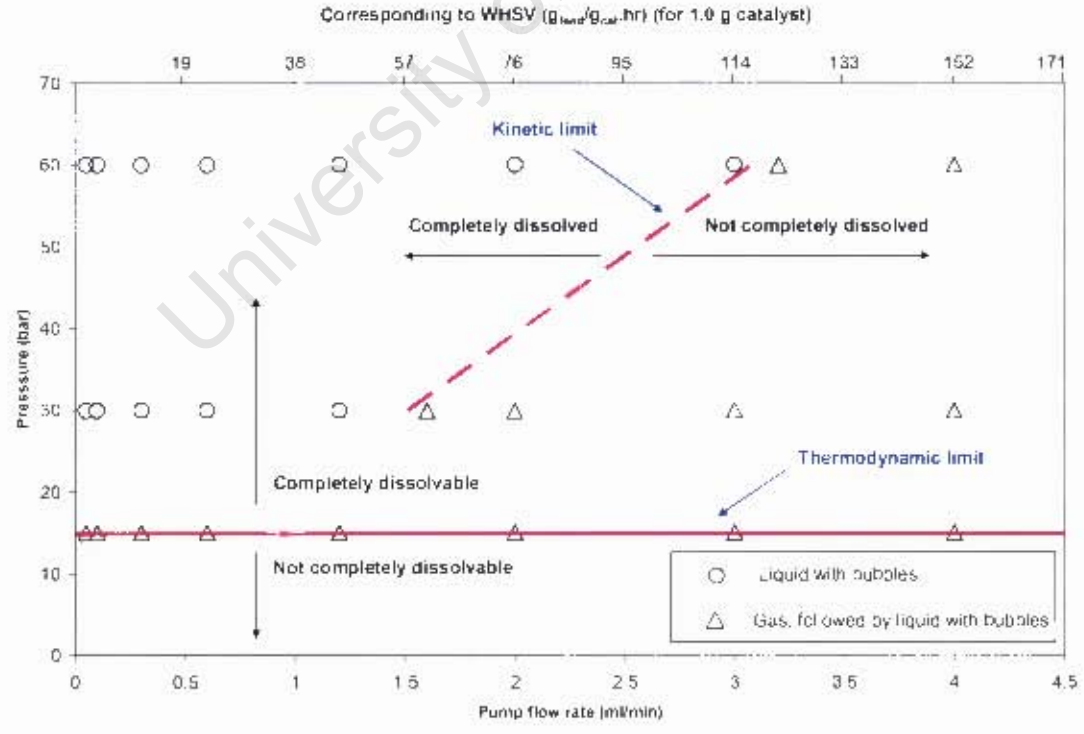

Figure 5.2 Solubility of hydrogen in 1-hexene as a function of pressure (bar) and feed flow rate (ml/min) at H_2/Oil molar ratio = 0.010 and 60 °C

Table 5.2 Hydrogenation runs performed and summary of major results[a] (reaction temperature was always 60 °C)

Run No.	Feed composition (mol % 1-hexyne in 1-hexene)	Apparatus arrangement	Catalyst mass (g)	Pressure (bar)	Pump Rate[g] (ml/min)	WHSV[b] ($g_{oil}/g_{cat}.hr$)	H_2/Oil molar	Hydrogen consumption[f, h] (%)	1-hexyne removal[h] (%)	Specificity [h]
1	1.0	1 dissolver, 1 reactor	1.0910[c]	30	0.2-0.35	7.0-12.2	0.01	61-67	22-23	103-179
2	1.0	1 dissolver, 1 reactor	1.0699	30	0.2-0.35	7.1-12.4	0.01	59-68	21-23	88-178
3	1.0	1 dissolver, 1 reactor	1.0910[c]	30	0.25-0.35	8.7-12.2	0.03	43-73	38-41	29-65
4	1.0	1 dissolver, 1 reactor	1.1075	10	0.2-0.35	6.9-12.8	0.01	91-97	11-12	17
5	1.0	1 dissolver, 2 reactors	1.0748 (reactor 1) 1.1093 (reactor 2)	30	0.2-0.35	3.5-6.1[i]	0.01	95-98	36-38	134-197
6	1.0	1 dissolver, 2 reactors	1.1186 (reactor 1) 1.1039 (reactor 2)	30 60	0.25-0.35 0.25	4.3-6.0 4.3[i]	0.03	92-98 89	47-48 81	26 91
7	1.0	2 dissolver / reactor stages Equal streams of H_2 added to each of the dissolvers	1.0889 (reactor 1) 1.0741 (reactor 2)	30	0.2-0.35	3.5-6.2[i]	0.01[d] (per dissolver)	86-89	63-64	125-142
8	1.0	2 dissolver / reactor stages Equal streams of H_2 added to each of the dissolvers	1.0889 (reactor 1) 1.0741 (reactor 2)	30 60	0.2-0.35 0.2	3.5-6.2[i] 3.5[i]	0.03[d] (per dissolver)	82-89 93	54-55 82	14 21
9	0.5	1 dissolver, 1 reactor	1.0910[c]	30	0.2-0.35	7.0-12.2	0.005	56-73	20-21	118-210
10	0.5	1 dissolver, 1 reactor	1.0910[c]	10	0.25-0.4	8.7-13.8	0.015	35-63	19-21	27-59
11	0.5	1 dissolver, 1 reactor	1.0910[c]	30	0.25-0.4	8.7-13.8	No H_2	-	0	-

[a] The runs are grouped according to the presence of undissolved hydrogen in the reactor (as per Figures 5.1 to 5.4) as follows:

- No hydrogen addition (black text)
- Hydrogen completely dissolved in the liquid phase (green text)
- Hydrogen partially undissolved in the liquid phase at the inlet of the reactor. However, according to product analysis hydrogen consumption was so that complete dissolution could have been achieved at the outlet. (light orange text) (discussed further in section 6.6.1)
- Hydrogen never completely dissolved in the liquid phase (red text)

[b] Varied varying the pump rate of the liquid and, simultaneously in equal measure, the H_2 flow rate. This measure also varied the linear velocity in the reactor (see footnote g)

[c] Referring to the total mass of catalyst in both the reactors together

[d] Same amount of hydrogen added to each of the dissolver/reactor stages

[e] Same catalyst charge utilised to carry out all of these runs

[f] Refers to the hydrogen and was calculated from the hydrocarbon distribution in the reactor effluent since the reactor effluent was not analysed for remaining hydrogen

[g] Pump rate (ml/min) is an indication of the linear velocity

[h] Averages from the individual samples attained at the given reaction conditions

5.2.2 Blank runs

A run was carried out with 0.5 mol % 1-hexyne in 1-hexene with one dissolver and one reactor at 30 bar, with no hydrogen addition (run 11). The purpose of this run was to show that there were no background reactions that occur at the absence of hydrogen such as isomerisation of 1-hexene or 1-hexyne. The results did demonstrate that there was no conversion of 1-hexene or 1-hexyne. Therefore, all activity observed can be attributed to the presence of hydrogen.

Brown (2005) conducted blank runs utilising only inert catalyst diluent (SiC) to investigate the occurrence of background reactions in the absence of catalyst. No hydrogenation or isomerisation of both 100 % 1-hexene feed and 5 mol% 1,5-hexadiene impurity in 1-hexene feed occurred at 15 bar, 60 °C and H_2/Oil molar ratio of 0.2. The catalyst diluent, the reactor walls and the tubing were therefore considered to be completely inert under typical operational conditions. Therefore, all activity observed was attributed to the presence of the catalyst.

5.2.3 Time-on-stream performance of catalyst

The time-on-stream behaviour of the catalyst was analysed plotting the conversion of 1-hexyne against time-on-stream at varying space velocities using the data obtained from runs 1 and 2 (figure 5.6). Within duration of the runs, only a slight decrease in impurity conversion was observed which could be ignored with respect to comparing the effect of varying reaction conditions.

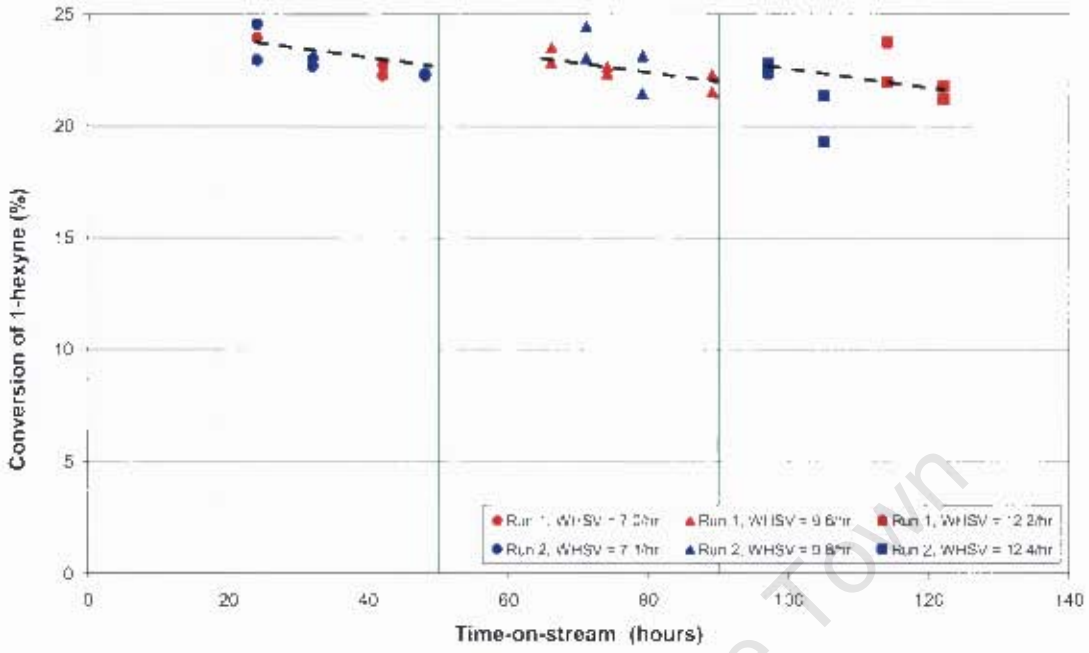

Figure 5.6 Time-on-stream performance of catalyst
(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)
(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

5.2.4 Repeatability

In order to determine the repeatability of results obtained from the experimental apparatus, it was necessary to undertake at least two runs under the same experimental conditions and similar catalyst loading (runs 1 and 2). All variables except space velocity were kept constant while the same set of space velocities was repeated. Figure 5.7 shows the conversion of the 1-hexyne impurity as a function of the loss of 1-hexene ("specificity plot"). Similar specificities were obtained for runs 1 and 2 at the different space velocities.

Impurity conversion was observed to be almost constant as a function of space velocity (or linear velocity) at 21-23 % but 1-hexene conversion increased (from 0.13 to around 0.24 %) with increasing space velocity that is more or less doubled when doubling space velocity, resulting in lower specificities.

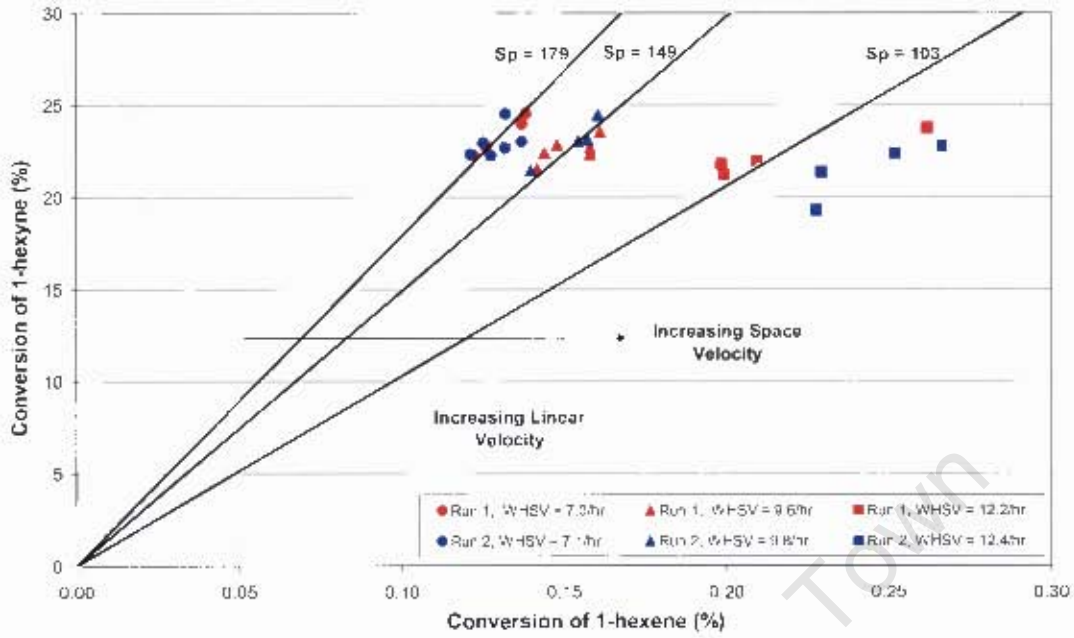

Figure 5.7 Specificity plot for experimental repeatability

(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

In figure 5.8 component molar fractions are plotted against space time (and correspondingly space velocity) for runs 1 and 2. It is observed that at high space times, the product molar composition does not change much. It should be noted that this is not due to hydrogen depletion (see figure 5.8) or thermodynamic limits (see section 5.3).

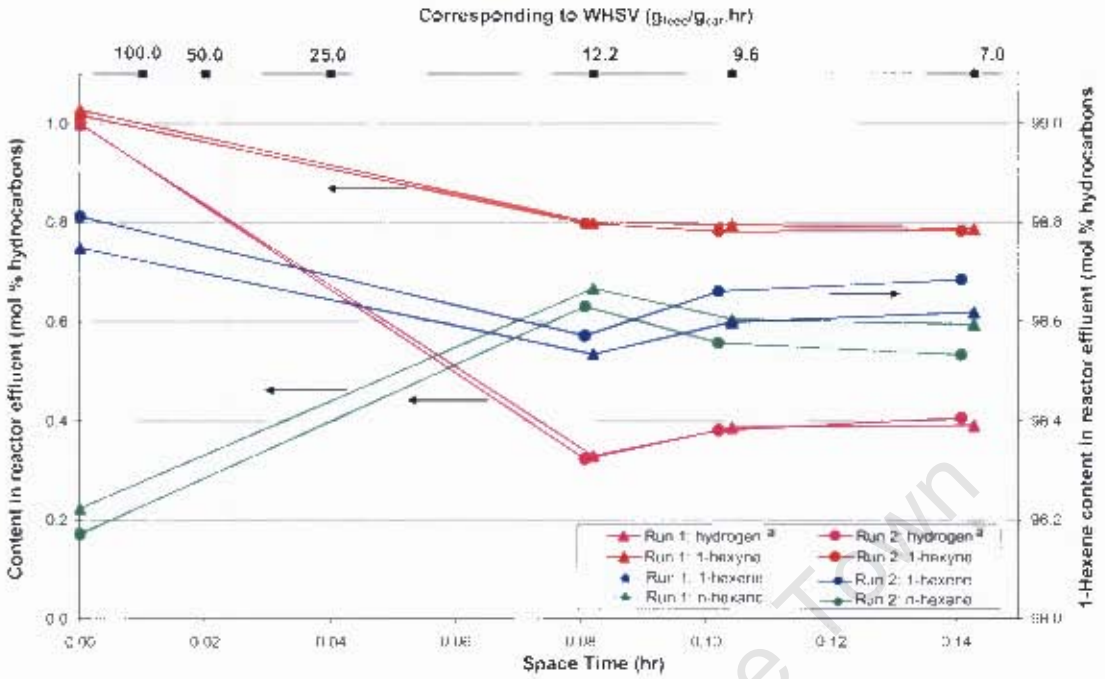

Figure 5.8 Relationship between space time and molar fractions of components[b] in the reactor effluent of runs 1 and 2. Zero space time corresponds to the feed composition (Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2) (Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

[a] *Calculated from the hydrocarbon distribution in the reactor effluent, referring to total reactor effluent. (see section 4.5.4.6)*

[b] *A full analysis of all the components present was not undertaken, as the unidentified peaks form less than 0.5 % of the feed and product samples. Most of these 'unknowns' had been present in the 1-hexene feed and have been found to be inert. The peaks of interest were thus that of the 1-hexyne, 1-hexene and n-hexane which have been considered to be the only components present.*

5.2.5 Variation of feed impurity concentration

The effect of varying the feed impurity concentration was investigated comparing runs 1 and 2 with a feed 1-hexyne concentration of 1 mol % (the data shown in figure 5.7) with run 9 with a feed 1-hexyne concentration of 0.5 mol % under the same test conditions. Conversions were varied at two different space velocities while maintaining all the other variables constant. The results are shown in figure 5.9. 1-Hexyne conversions of 20-21 %, 1-hexene conversions of 0.09-0.18 % and thus specificities of 118 and 210 (dashed lines) were observed at the lower impurity content which are slightly higher than those obtained at 1 mol% 1-hexyne content. It should be noted that 1-hexene conversion increased with increasing space velocity.

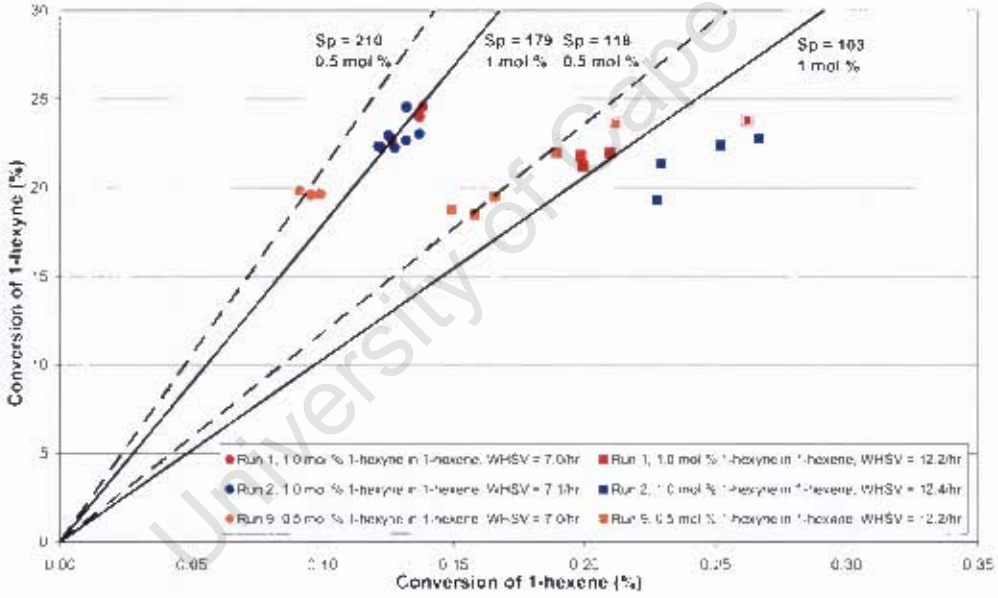

Figure 5.9 Specificity plot for variation of feed impurity concentration

(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

(Run 9: 0.5 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.005, 1 dissolver, 1 reactor, catalyst mass: 1.090 g Pd-Ag/TiO_2)

5.2.6 The effect of undissolved hydrogen in the reactor

In run 3 the same conditions as in runs 1 and 2 were kept except that the H_2/Oil molar ratio was increased to 0.03. At this condition, according to figure 5.4 and table 5.2, there was undissolved hydrogen present in the first part of the reactor since the H_2/Oil feed ratio was beyond the thermodynamic limit at the reaction pressure of 30 bar. Also, the higher the flow rate, the less hydrogen may have actually dissolved. However, product analyses show that hydrogen consumption was high enough to have the H_2/Oil ratio lowered to a level not exceeding the thermodynamic limit. Higher 1-hexyne but in particular higher 1-hexene conversions were observed compared to runs 1 and 2 (38-41% and 0.59-1.44% respectively) so that specificities were lower (29-65) than in runs 1 and 2 (figure 5.10, dashed lines). It should be noted that 1-hexene conversion increased with increasing space velocity.

In run 4 the same conditions as in runs 1 and 2 were kept i.e. a molar H_2/Oil ratio of 0.01, except that the pressure was decreased to 10 bar. At this condition, according to figure 5.2 and table 5.2, there was also undissolved hydrogen present in the first part of the reactor and the rest of the hydrogen completely dissolved at the reactor outlet. Lower 1-hexyne conversion was observed (11-12%) compared to runs 1 and 2 but higher 1-hexene conversion (0.68-0.74%) so that the specificity dropped to 17 (figure 5.10, dotted lines).

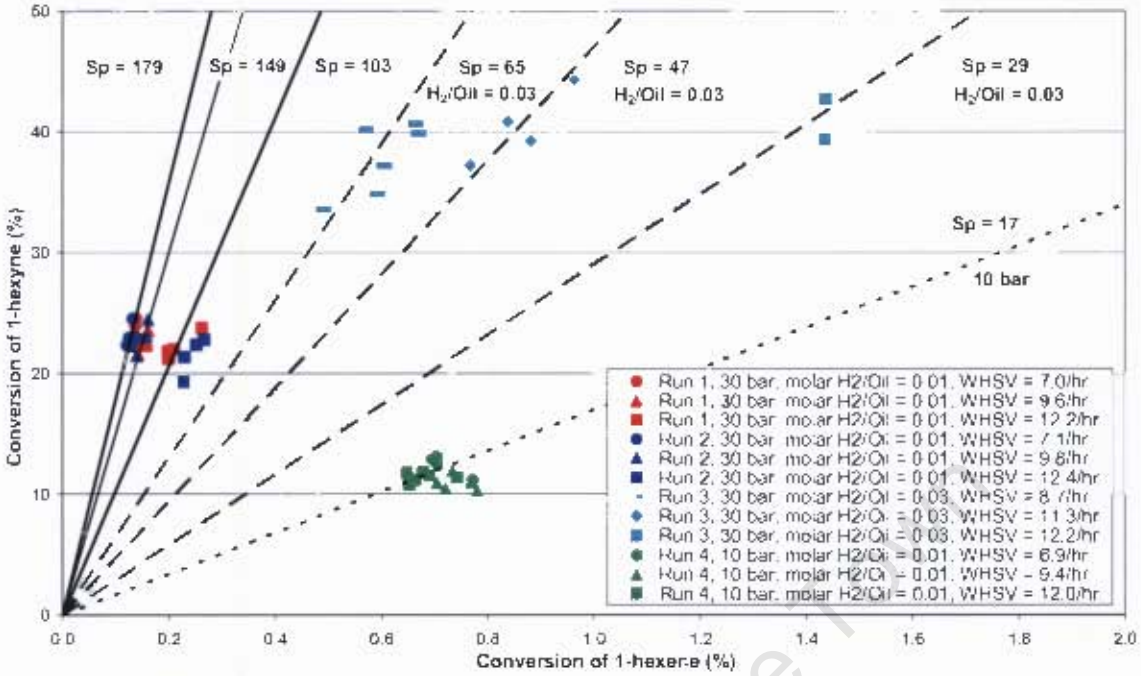

Figure 5.10 Specificity plot for the effect of dissolved and undissolved hydrogen in the reactor

(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

(Run 3: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.03, 1 dissolver, 1 reactor, catalyst mass: 1.090 g Pd-Ag/TiO_2)

(Run 4: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 10 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.1075 g Pd-Ag/TiO_2)

The effect of the feed molar H_2/impurity ratio on product composition is shown in figure 5.11, where the molar composition of the feed is compared to the molar compositions of the products from runs 1, 2 and 3 at the same linear velocity of 0.35 ml/min and the same pressure of 30 bar. The results indicate that an increase of the molar H_2/impurity ratio lead to further conversion of 1-hexyne, increased n-hexane yield and lower amount of 1-hexene. This result may be compared to the equilibrium composition in section 5.3.

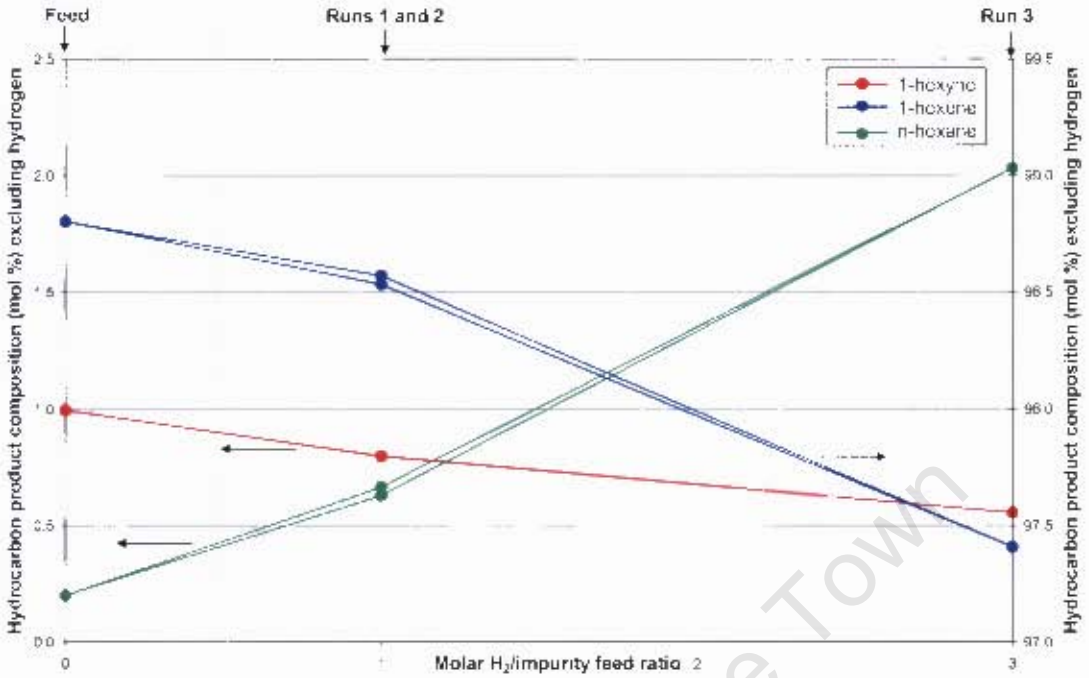

Figure 5.11 Molar composition[3] of the reactor effluent as a function of feed molar H_2/impurity ratio

(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

(Run 3: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.03, 1 dissolver, 1 reactor, catalyst mass: 1.090 g Pd-Ag/TiO_2)

[3] *A full analysis of all the components present was not undertaken, as the unidentified peaks form less than 0.5 % of the feed and product samples. Most of these 'unknowns' had been present in the 1-hexene feed and have been found to be inert. The peaks of interest were thus that of the 1-hexyne, 1-hexene and n-hexane which have been considered to be the only components present.*

5.2.7 One dissolver and two reactors with no inter-stage hydrogen addition (large reactor mode)

In run 5, a second reactor charged with the same quantity of catalyst, was added with no inter-stage hydrogen addition. This arrangement allowed the unreacted hydrogen from the first reactor a second opportunity to react and thus this arrangement is equivalent to a single large reactor. Figure 5.2 and table 5.2 indicate that at the low molar H_2/Oil ratio and low pump rates utilised in this run, the hydrogen was completely dissolved in the liquid phase. The results indicated higher impurity conversions (36-38%) in comparison to runs 1 and 2 and a proportional increase in 1-hexene conversion (to 0.19-0.27%) so that specificities remained high and almost constant (134-197) (figure 5.12, dashed lines).

Run 6 was initially run analogous to run 5, except that the H_2/Oil molar ratio was increased to 0.03. Figure 5.4 and table 5.2 indicate that at this condition, at 30 bar, the system operated below the thermodynamic limit so that there was undissolved hydrogen at least in the first reactor. The results indicated higher impurity conversions (47-48 %) in comparison to run 5 but also much higher 1-hexene conversion (1.79-1.91 %), so that specificities obtained were significantly lower (26) than those obtained in run 5 (figure 5.12, dotted line).

Thereafter the pressure was increased to 60 bar. The effect of this alteration was to overcome the thermodynamic limitation while at WHSV = 4.3 $g_{oil}/g_{cat}.hr$ the dissolver was also operating within the kinetic limit and thus to get all of the hydrogen dissolved in the liquid phase, as per figure 5.4 and table 5.2. The result of this change was an increase in the impurity conversion to 83% and a significant decrease in 1-hexene conversion to 0.94 % resulting in a significant increase in specificity, compared to the 30 bar condition, to 91 (figure 5.12, dot-dashed line).

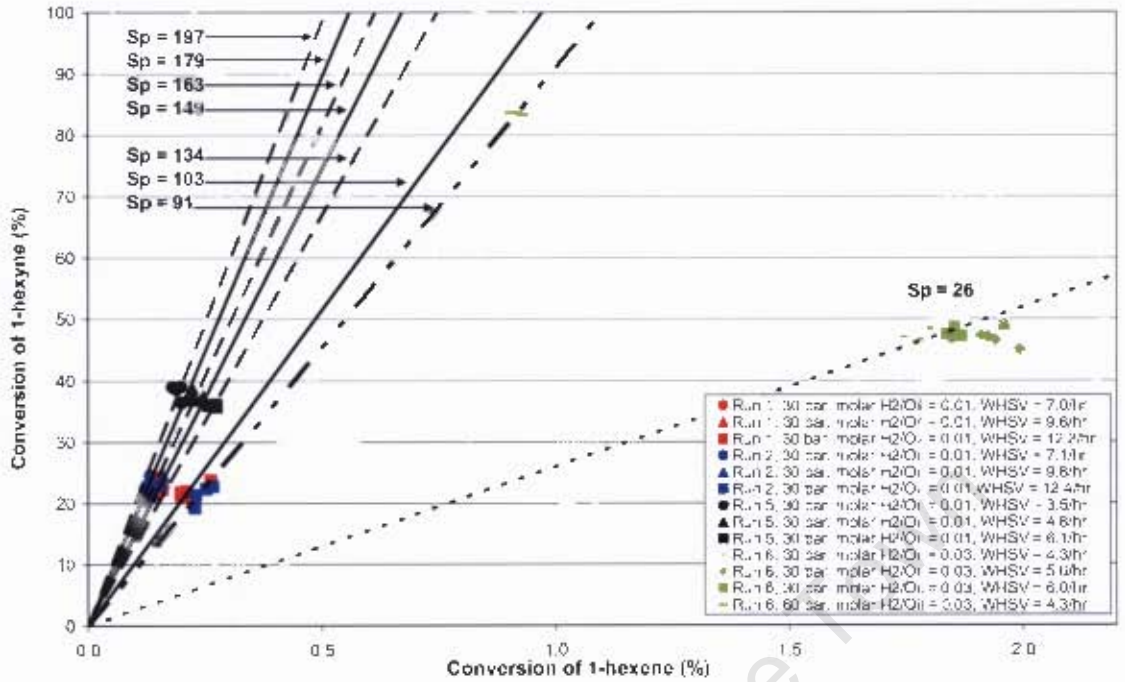

Figure 5.12 Specificity plot for one dissolver and two reactors with no inter-stage hydrogen addition (large reactor mode)

(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

(Run 5: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 2 reactors, catalyst mass: 1.0748 g Pd-Ag/TiO_2 in first reactor, 1.1093 g Pd-Ag/TiO_2 in second reactor)

(Run 6: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 and 60 bar, molar H_2/Oil = 0.03, 1 dissolver, 2 reactors, catalyst mass: 1.1186 g Pd-Ag/TiO_2 in first reactor, 1.1039 g Pd-Ag/TiO_2 in second reactor)

In figure 5.13, component molar fractions are plotted against space time (and correspondingly space velocity) for run 5. As with runs 1 and 2 (see figure 5.8) it is observed that at high space times, the product composition does not change much. It should be noted that this is not due to hydrogen depletion (see figure 5.13) or thermodynamic limits (see section 5.3).

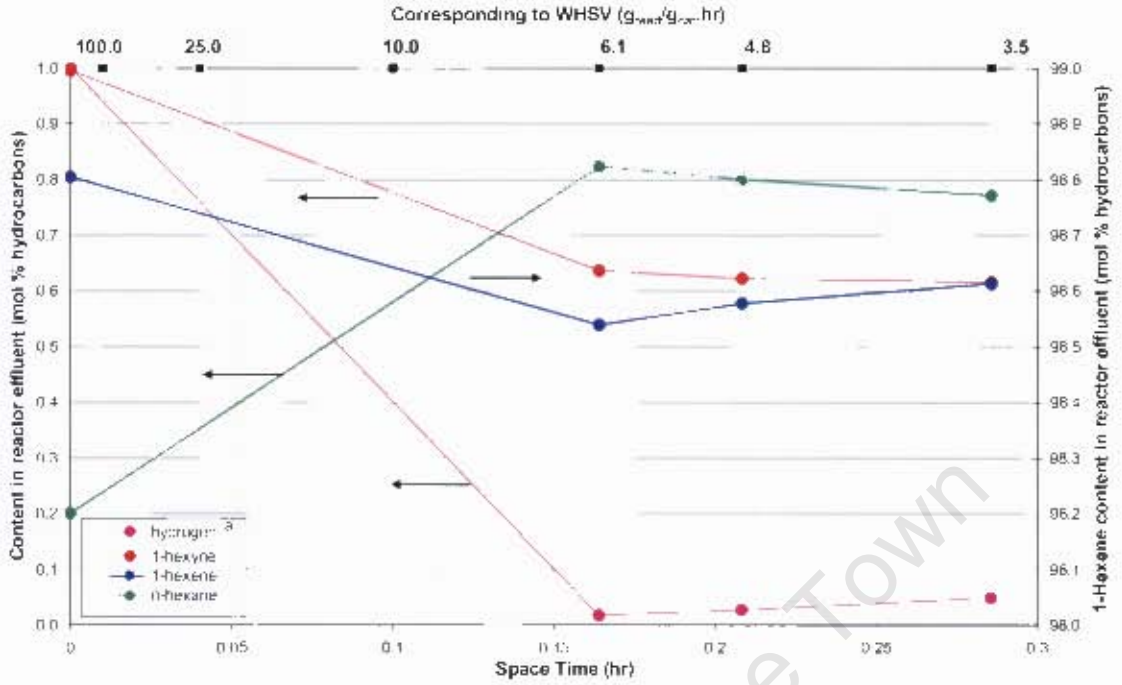

Figure 5.13 Relationship between space time and molar fractions of components[b] in the reactor effluent of run 5. Zero space time corresponds to the feed composition (Run 5: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 2 reactors, catalyst mass: 1.0748 g Pd-Ag/TiO_2 in first reactor, 1.1093 g Pd-Ag/TiO_2 in second reactor)

[a] Calculated from the hydrocarbon distribution in the reactor effluent, referring to total reactor effluent (see section 4.5.4.6)

[b] A full analysis of all the components present was not undertaken, as the unidentified peaks form less than 0.5 % of the feed and product samples. Most of these 'unknowns' had been present in the 1-hexene feed and have been found to be inert. The peaks of interest were thus that of the 1-hexyne, 1-hexene and n-hexane which have been considered to be the only components present.

The effect of the addition of a second reactor stage on product composition is shown in figure 5.14, where the molar composition of the feed is compared to the molar compositions of the products from runs 1, 2 and 5 at the same linear velocity of 0.35 ml/min and the same pressure of 30 bar. The results indicate that the addition of the second reactor stage lead to further conversion of 1-hexyne and hydrogen, increased n-hexane yield and an almost unchanged amount of 1-hexene.

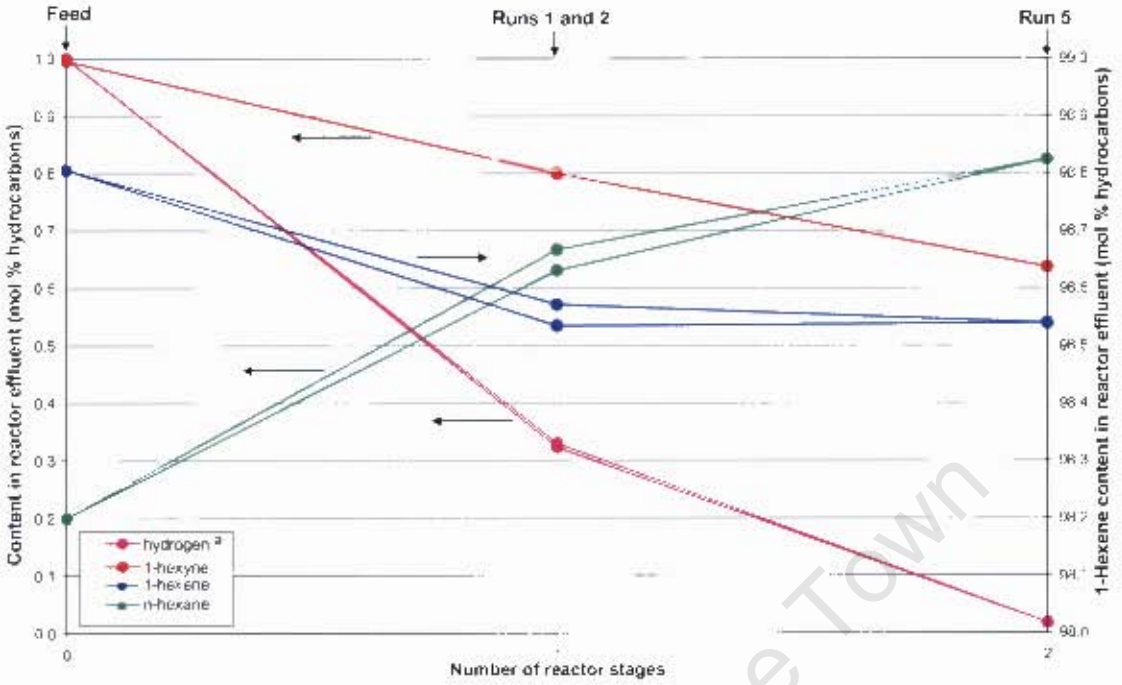

Figure 5.14 Molar composition[b] of the reactor effluent as a function of number of reactor stages

(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

(Run 5: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 2 reactors, catalyst mass: 1.0748 g Pd-Ag/TiO_2 in first reactor, 1.1093 g Pd-Ag/TiO_2 in second reactor)

[a] *Calculated from the hydrocarbon distribution in the reactor effluent, referring to total reactor effluent (see section 4.5.4.6)*

[b] *A full analysis of all the components present was not undertaken, as the unidentified peaks form less than 0.5 % of the feed and product samples. Most of these 'unknowns' had been present in the 1-hexene feed and have been found to be inert. The peaks of interest were thus that of the 1-hexyne, 1-hexene and n-hexane which have been considered to be the only components present.*

5.2.8 Two dissolver / reactor stages with inter-stage hydrogen addition (dual stage mode)

In run 7, the dissolver and reactor pair was followed by a second dissolver with further hydrogen addition and a second reactor. The H_2/Oil molar ratio of 0.01 utilised in the first stage and the low pump rate allowed, according to figure 5.2, complete dissolution of hydrogen in the liquid phase in the first reactor. Another hydrogen stream with the same flow was added to the second dissolver. Assuming more than 50% hydrogen consumption in the first reactor (as can be derived from runs 1 and 2, see table 5.2) the total H_2/Oil molar ratio in the second dissolver was < 0.015 and according to figure 5.3 this quantity should have completely dissolved in the oil. Results showed significantly higher impurity conversions (63-64 %) in comparison to run 5 ('large reactor' without intermediate hydrogen addition) and an almost proportional increase in 1-hexene conversion (0.45-0.51 %) resulting indeed in specificities that were almost equal to those obtained in run 5 (125-142) (figure 5.15, dashed lines).

Run 8 was set up analogous to run 7, at 30 bar, except that the H_2/Oil molar ratio in the first stage was increased to 0.03 and the same amount was further added to the second stage. At the H_2/Oil molar ratios utilised, according to figure. 5.4 and the results of run 3, see figure 5.10, there was undissolved hydrogen in both reactors. The results (figure 5.15, dotted line) indicated slightly lower impurity conversions (54-55 %) but much higher 1-hexene conversions (3.86-4.28 %) in comparison to run 7, and the specificities obtained were, consequently, much lower (14) than those obtained in run 7.

Thereafter the pressure was increased to 60 bar. This allowed the hydrogen in the first dissolver to dissolve completely, as can be derived from figure 5.4, and the rather high specificities obtained from run 6 ('large reactor' without intermediate hydrogen addition) at 60 bar (figure 5.12, dot-dashed line). However, the hydrogen stream added to the second dissolver may not have dissolved completely. The result of this increase in pressure increased impurity conversion to 82 %, while 1-hexene conversion was almost unaffected (4.0 %). Compared to run 6

(dot-dashed line in figure 5.12), the additional, undissolved hydrogen did not result in a change of impurity conversion but a significant increase in 1-hexene conversion so that specificities decreased to 21 (dot-dashed line in figure 5.15).

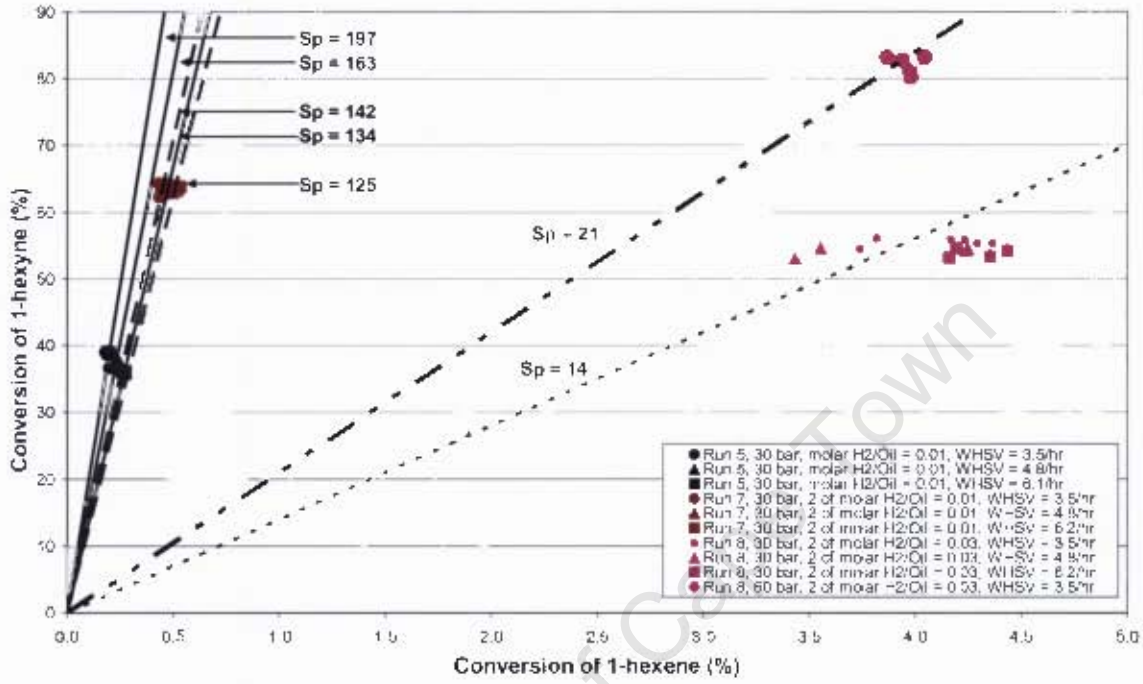

Figure 5.15 Two dissolver / reactor stages with inter-stage hydrogen addition (dual stage mode)

(Run 5: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 2 reactors, catalyst mass: 1.0748 g Pd-Ag/TiO_2 in first reactor, 1.1093 g Pd-Ag/TiO_2 in second reactor)

(Run 7: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01 to each of the dissolvers, 2 dissolver / reactor stages, half of the H_2 added to each of the dissolvers, catalyst mass: 1.0889 g Pd-Ag/TiO_2 in first reactor, 1.0741 g Pd-Ag/TiO_2 in second reactor)

(Run 8: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 and 60 bar, molar H_2/Oil = 0.03 to each of the dissolvers, 2 dissolver / reactor stages, half of the H_2 added to each of the dissolvers, catalyst mass: 1.0889 g Pd-Ag/TiO_2 in first reactor, 1.0741 g Pd-Ag/TiO_2 in second reactor)

In figure 5.16, component molar fractions are plotted against space time (and correspondingly space velocity) for run 7. As with runs 1, 2 and 5 (see figures 5.8 and 5.13); it is observed that at high space times, the product composition does not change much. It should be noted that this is not due to hydrogen depletion (see figure 5.16) or thermodynamic limits (see section 5.3).

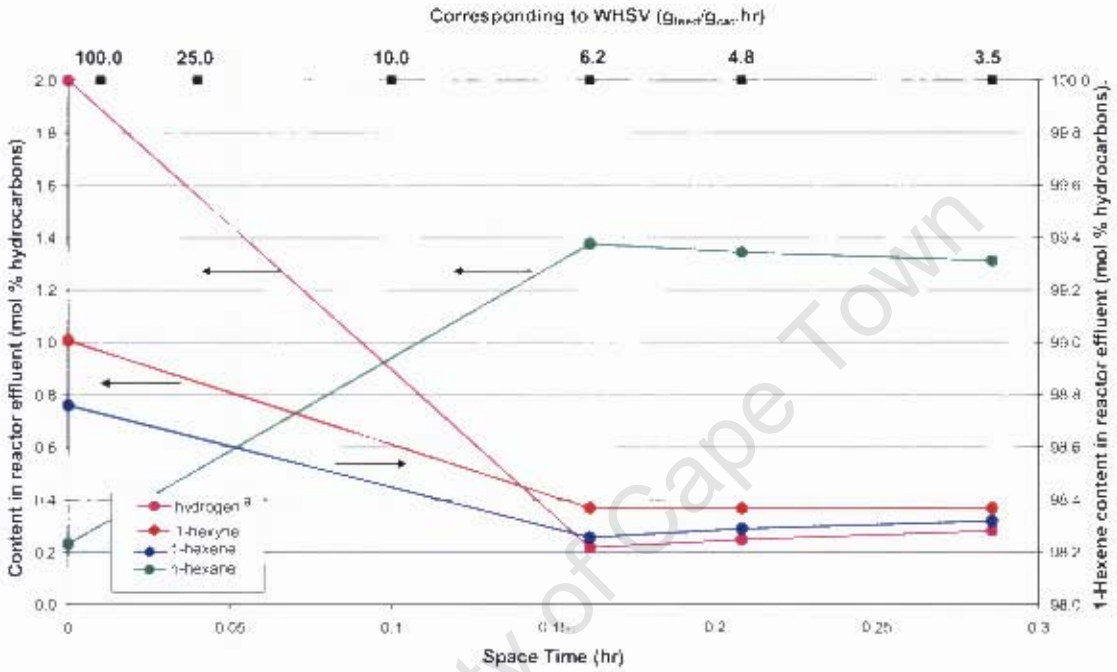

Figure 5.16 Relationship between space time and molar fractions of components[b] in the reactor effluent of run 7. Zero space time corresponds to the feed composition (Run 7: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01 to each of the dissolvers, 2 dissolver / reactor stages, half of the H_2 added to each of the dissolvers, catalyst mass: 1.0889 g Pd-Ag/TiO_2 in first reactor, 1.0741 g Pd-Ag/TiO_2 in second reactor)

[a] *Calculated from the hydrocarbon distribution in the reactor effluent, referring to total reactor effluent (see section 4.5.4.6)*

[b] *A full analysis of all the components present was not undertaken, as the unidentified peaks form less than 0.5 % of the feed and product samples. Most of these 'unknowns' had been present in the 1-hexene feed and have been found to be inert. The peaks of interest were thus that of the 1-hexyne, 1-hexene and n-hexane which have been considered to be the only components present.*

The effect of interstage hydrogen addition is shown in figure 5.17, where the molar composition of the feed is compared to the molar composition of the products from runs 1, 2, 5 and 7 at the same linear velocity of 0.35 ml/min and the same pressure of 30 bar. The results indicate that the addition of interstage hydrogen, in comparison to run 5 ('large reactor' without intermediate hydrogen addition), lead to an almost linear increase in 1-hexyne conversion, a significant increase in 1-hexene conversion and a corresponding increase in n-hexane yield.

5.2.9 The effect of hydrogen dissolution at lower impurity concentrations

Run 9 was carried out in single stage mode analogous to runs 1 and 2 except that the impurity concentration was decreased to 0.5 mol %, and the H_2/Oil molar ratio was lowered to 0.005, so that the molar H_2/impurity ratio was unchanged. The pressure was maintained correspondingly at 30 bar so that for the low pump rates utilised all hydrogen was dissolved in the liquid phase (figure 5.1). The results indicated impurity conversions (20-21 %), 1-hexene conversions (0.09-0.18 %) and thus specificities (118-210) similar to runs 1 and 2 (figure 5.18, dashed lines).

In run 10 the same conditions as in run 9 were maintained except that the H_2/Oil molar ratio was increased to 0.015. The pressure was maintained at 30 bar. For the low pump rates utilised hydrogen dissolution in the liquid phase was on the edge of the operating window, close to the thermodynamic limit and at the highest pump rate (highest WHSV) also close to the kinetic limit (figure 5.3). The results indicated slightly lower impurity conversions (18-21 %) compared to run 9 but much higher 1-hexene conversions (0.34-0.77 %) and, therefore, much lower specificities (27-55) (figure 5.18, dotted lines). It should be noticed that 1-hexene conversion increased with increasing space velocity.

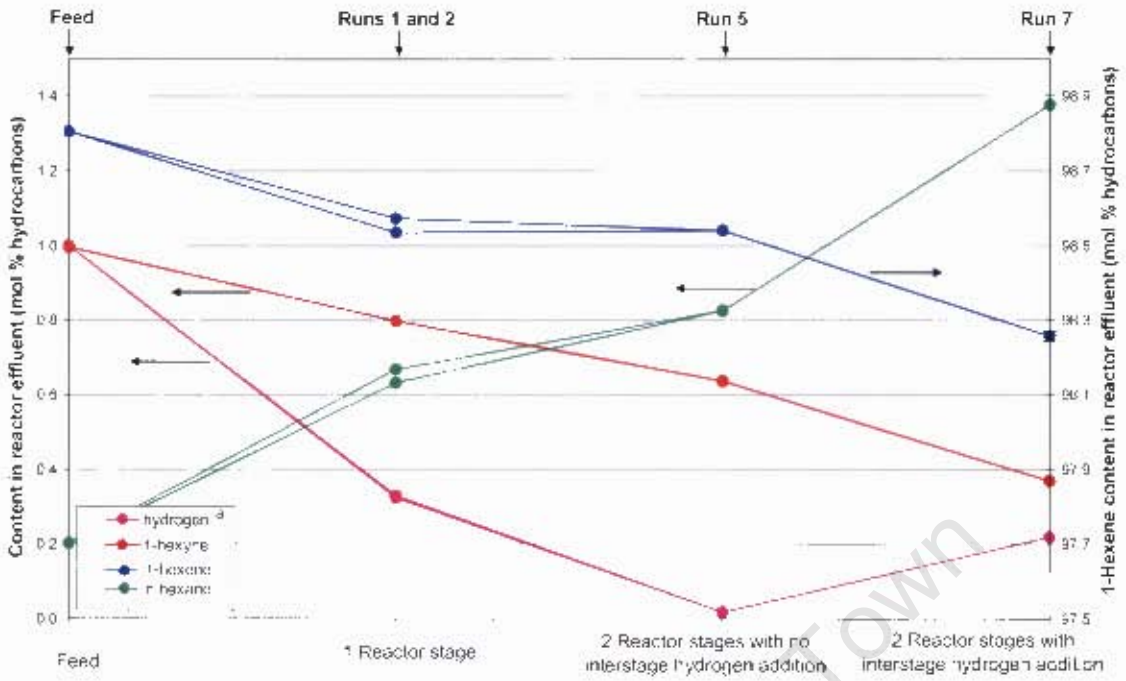

Figure 5.17 Molar composition[b] of the reactor effluent as a function of number of reactor stages and interstage hydrogen addition

(Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

(Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2)

(Run 5: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 2 reactors, catalyst mass: 1.0748 g Pd-Ag/TiO_2 in first reactor, 1.1093 g Pd-Ag/TiO_2 in second reactor)

(Run 7: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01 to each of the dissolvers, 2 dissolver / reactor stages, half of the H_2 added to each of the dissolvers, catalyst mass: 1.0889 g Pd-Ag/TiO_2 in first reactor, 1.0741 g Pd-Ag/TiO_2 in second reactor)

[a] *Calculated from the hydrocarbon distribution in the reactor effluent, referring to total reactor effluent (see section 4.5.4.6)*

[b] *A full analysis of all the components present was not undertaken, as the unidentified peaks form less than 0.5 % of the feed and product samples. Most of these 'unknowns' had been present in the 1-hexene feed and have been found to be inert. The peaks of interest were thus that of the 1-hexyne, 1-hexene and n-hexane which have been considered to be the only components present.*

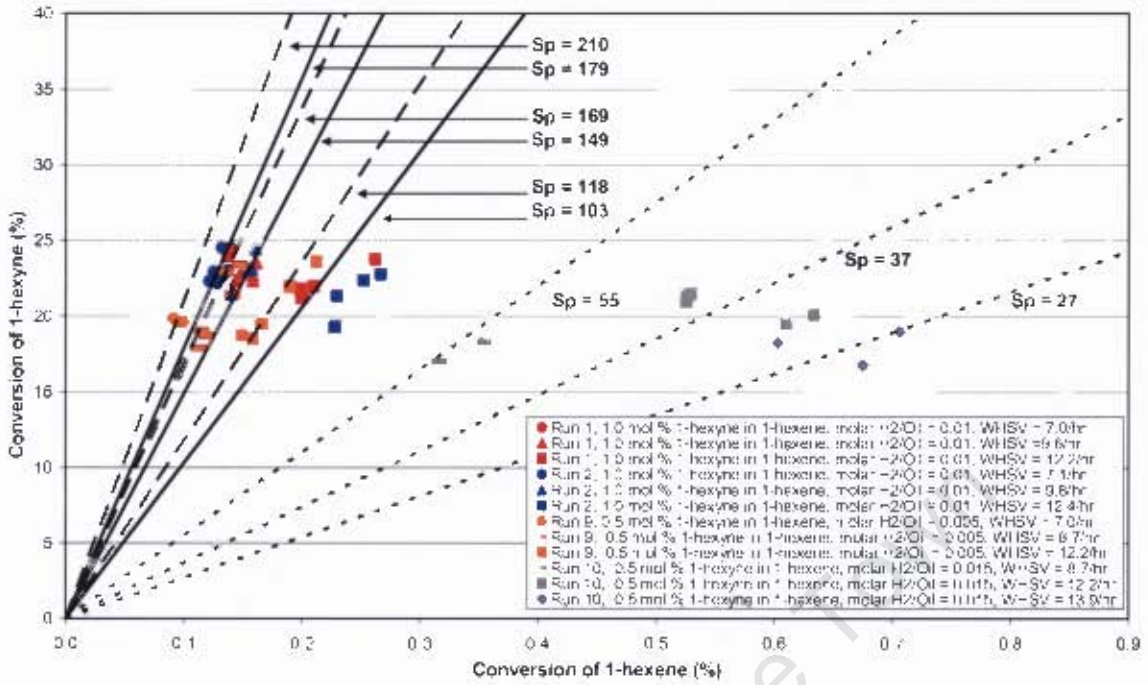

Figure 5.18 The effect of hydrogen dissolution at lower impurity concentrations (Run 1: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2) (Run 2: 1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2) (Run 9: 0.5 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.005, 1 dissolver, 1 reactor, catalyst mass: 1.090 g Pd-Ag/TiO_2) (Run 10: 0.5 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.015, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

5.2.10 The effect of linear velocity on hydrogen consumption, 1-hexyne and 1-hexene conversion

The effect of linear velocity on hydrogen consumption, 1-hexyne and 1-hexene conversions is given in figures 5.19-5.21 for all runs. The linear velocity is varied by varying the liquid feed pump rate (ml/min) that is space velocity, while varying the hydrogen flow rate simultaneously. Hydrogen consumption is given as a percentage of the amount fed. Trivially, the variation of hydrogen consumption is small at very high levels. However, the general trend of increasing hydrogen consumption and increasing 1-hexyne and 1-hexene conversions with increasing

space velocity (see arrows in the left sections of the figures), is contrary to expectations, as it is expected that lower space velocities, that is longer residence times, would allow for higher hydrogen consumption and higher 1-hexyne and 1-hexene conversions. When regarding the first data point from run 8 as an outlier (in brackets) then it appears that in runs with the higher H_2/Oil ratio of 0.03 (runs 3, 6 and 8) the unexpected effect is even stronger.

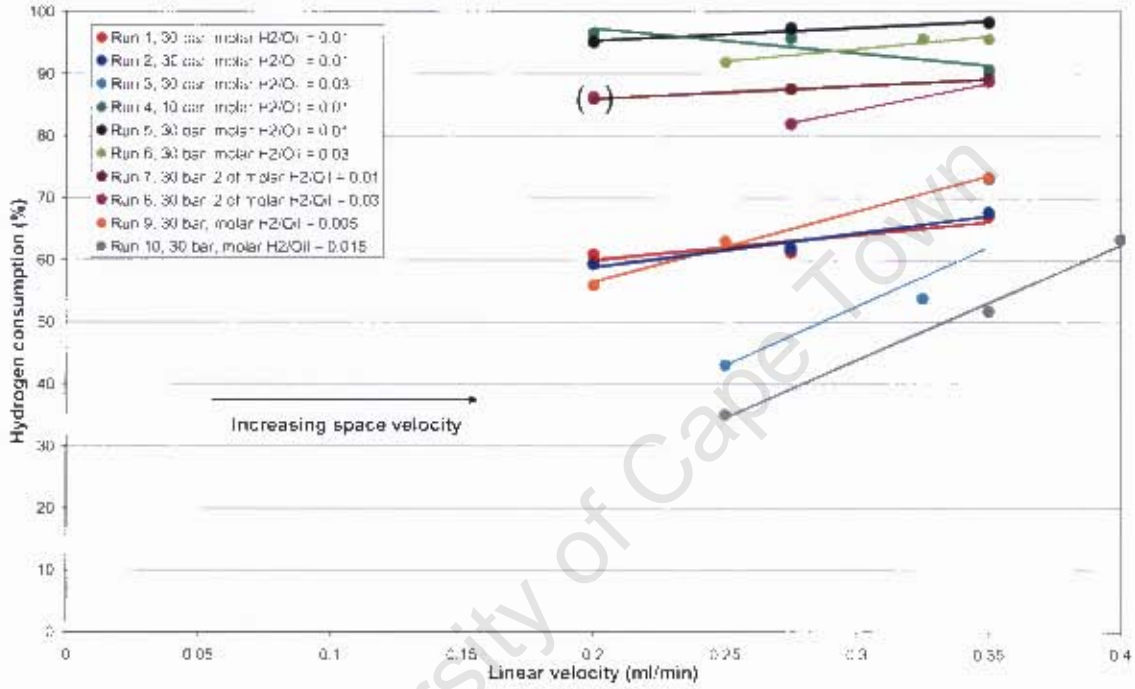

Figure 5.19 The effect of linear velocity on hydrogen consumption for all runs

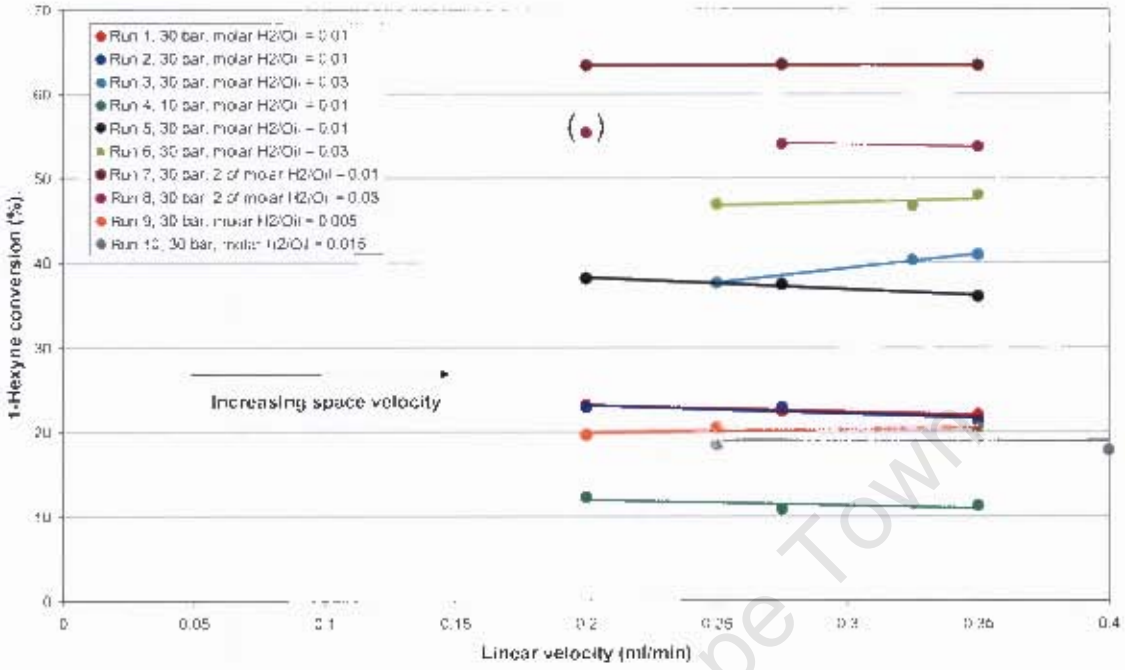

Figure 5.20 The effect of linear velocity on 1-hexyne conversion for all runs

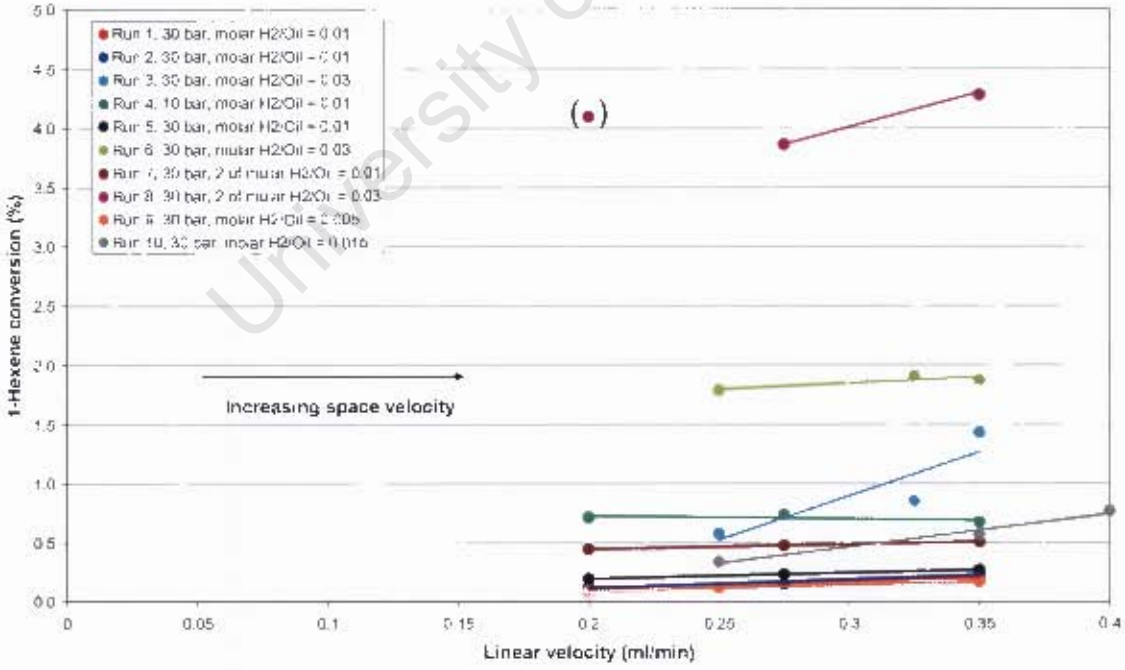

Figure 5.21 The effect of linear velocity on 1-hexene conversion for all runs

5.3 Thermodynamic equilibrium between 1-hexyne, 1-hexene, n-hexane and hydrogen

Aspen Plus was utilised to simulate the equilibrium between 1-hexyne, 1-hexene, n-hexane and hydrogen at several of the reaction conditions that were tested experimentally. A reactor model was utilised that calculated simultaneous phase and chemical equilibria. The reaction scheme modelled is given below. 1-Hexyne is hydrogenated to 1-hexene. 1-Hexene is hydrogenated to n-hexane.

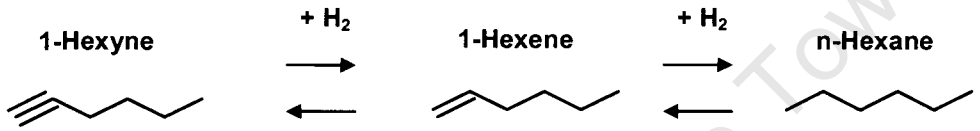

Figure 5.22 Equilibrium reaction scheme modelled in Aspen Plus

The method utilised for calculating the properties of the individual components was the Predictive Redlich-Kwong-Soave equation of state. Each feed stream was characterized by the H_2/Oil and H_2/impurity ratios. The temperature for all simulations was 60 °C. The pressure was varied as 10, 30 and 60 bar. Several simulations were performed with the molar product distributions given in table 5.3.

Table 5.3a shows that in equilibrium "all" hydrogen would be consumed and almost all of the 1-hexyne. Table 5.3b shows that the major product would be 1-hexene in case of molar H_2/impurity ratios of 1 and lower i.e. with an equimolar and sub-equimolar amount of hydrogen, but n-hexane in case of molar H_2/impurity ratios higher than equimolar.

The specificities calculated in each case are the 'thermodynamic specificities', i.e. the specificities expected at equilibrium. Since, there is a small net gain in 1-hexene in some cases, the 'conversion of 1-hexene' is negative, which results in large negative 'thermodynamic specificities'.

Table 5.3 Thermodynamic equilibrium of 1-hexyne, 1-hexene, n-hexane and hydrogen at various reaction conditions (60 °C)

a) Total feed and product (including hydrogen)

Molar H_2/Oil	Molar Impurity/Oil	Molar H_2/Impurity	Pressure (bar)	Feed composition (mole fraction)			Product composition (mole fraction)			
				1-hexene	hydrogen	1-hexyne	1-hexene	hydrogen	1-hexyne	n-hexane
0.01	0.01	1.00	10	0.98020	0.00990	0.00990	0.99917	0.00000	0.00042	0.00042
0.0025	0.01	0.25	30	0.98753	0.00249	0.00998	0.99245	0.00000	0.00752	0.00002
0.005	0.01	0.50	30	0.98507	0.00498	0.00995	0.99493	0.00000	0.00503	0.00003
0.01	0.01	1.00	30	0.98020	0.00990	0.00990	0.99917	0.00000	0.00042	0.00042
0.015	0.01	1.50	30	0.97537	0.01478	0.00985	0.99490	0.00000	0.00003	0.00506
0.02	0.01	2.00	30	0.97059	0.01961	0.00980	0.98996	0.00000	0.00002	0.01002
0.03	0.01	3.00	30	0.96117	0.02913	0.00971	0.97996	0.00000	0.00001	0.02003
0.03	0.01	3.00	60	0.96117	0.02913	0.00971	0.97996	0.00000	0.00001	0.02003
0.005	0.005	1.00	30	0.99005	0.00498	0.00498	0.99917	0.00000	0.00042	0.00042
0.015	0.005	3.00	30	0.98030	0.01478	0.00493	0.98996	0.00000	0.00002	0.01002

b) Hydrocarbon feed and product (excluding hydrogen)

Molar H_2/Oil	Molar Impurity/Oil	Molar H_2/Impurity	Pressure (bar)	Feed composition (mole fraction)		Product composition (mole fraction)			Conversion of 1-hexyne	Conversion of 1-hexene	Specificity
				1-hexene	1-hexyne	1-hexene	1-hexyne	n-hexane			
0.01	0.01	1.00	10	0.99000	0.01000	0.99917	0.00042	0.00042	95.8	-0.9	-103
0.0025	0.01	0.25	30	0.99000	0.01000	0.99245	0.00752	0.00002	24.8	-0.2	-100
0.005	0.01	0.50	30	0.99000	0.01000	0.99493	0.00503	0.00003	49.7	-0.5	-100
0.01	0.01	1.00	30	0.99000	0.01000	0.99917	0.00042	0.00042	95.8	-0.9	-104
0.015	0.01	1.50	30	0.99000	0.01000	0.99490	0.00003	0.00506	99.7	-0.5	-201
0.02	0.01	2.00	30	0.99000	0.01000	0.98996	0.00002	0.01002	99.8	0.0	27785
0.03	0.01	3.00	30	0.99000	0.01000	0.97996	0.00001	0.02003	99.9	1.0	99
0.03	0.01	3.00	60	0.99000	0.01000	0.97996	0.00001	0.02003	99.9	1.0	99
0.005	0.005	1.00	30	0.99500	0.00500	0.99917	0.00042	0.00042	91.7	-0.4	-219
0.015	0.005	3.00	30	0.99500	0.00500	0.98996	0.00002	0.01002	99.7	0.5	197

The equilibrium data from table 5.3b, for a feed of 1.0 mol% 1-hexyne in 1-hexene at 30 bar and 60 °C may be utilised to plot the variation of the product composition as a function of the H_2/impurity ratio. It should be noted that according to the data in table 5.3b, the almost straight lines in figure 5.23 are real.

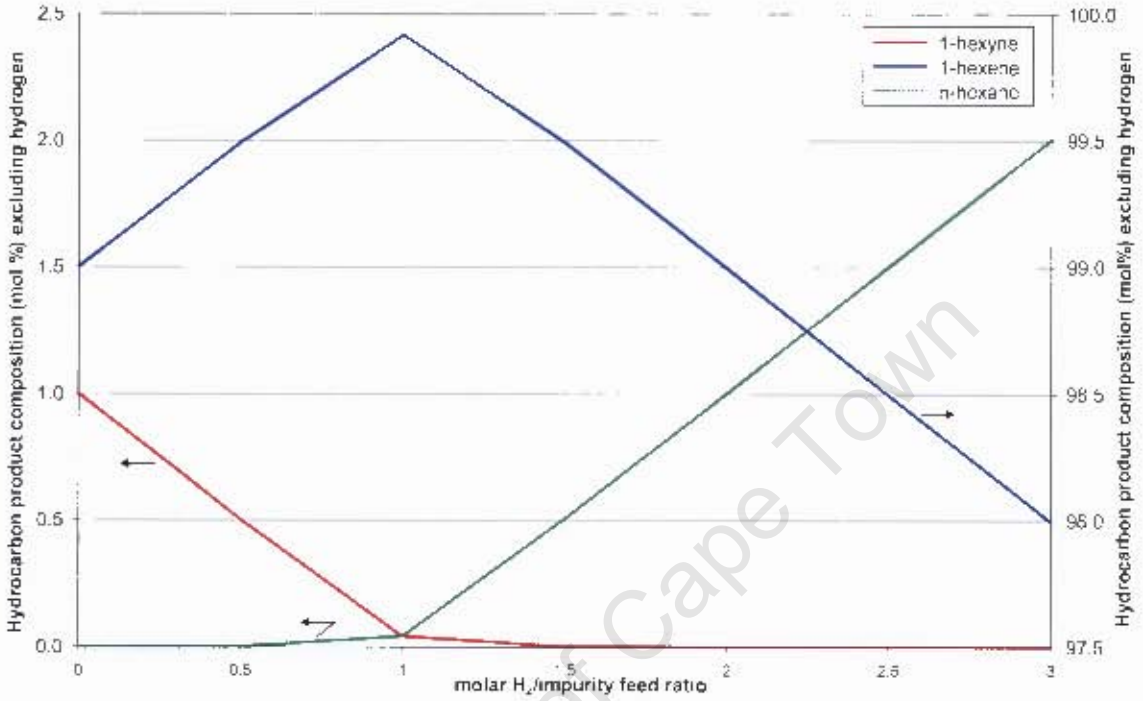

Figure 5.23 Product composition (molar) as a function of molar H_2/impurity feed ratio at thermodynamic equilibrium

Up to a molar H_2/impurity ratio of 1, there is a sharp decrease in 1-hexyne concentration, a sharp increase in 1-hexene yield and slight increase in n-hexane yield as H_2/impurity ratio is increased. However, above a molar H_2/impurity ratio of 1 when the mixture is depleted of 1-hexyne, this trend is reversed, as n-hexane is now the preferred reaction product leading to a steep incline in n-hexane yield and a sharp decrease in 1-hexene concentration. The yield of 1-hexene peaks at a molar H_2/impurity ratio of 1, while above a molar H_2/impurity ratio of 2, there is a net loss of 1-hexene. Impurity concentration is thus down from 1 mol % in the feed to 0.042 mol % corresponding to 95.8 % impurity equilibrium conversion. At a molar H_2/impurity ratio of 1.5, 1-hexyne equilibrium conversion is 99.7% so that any further increase in H_2/impurity ratio can not effect much further conversion. The effect of the feed H_2/impurity molar ratio is comparable to the results obtained in runs 1,2 and 3, as depicted in figure 5.11.

6 DISCUSSION

Reaction conditions for the individual runs and the major results are compiled in table 5.2. Run numbers refer also to table 5.2.

6.1 Improved analysis technique

Discrepancies in the hydrogen balance in previous work *(Brown, 2005)* indicated inaccuracies in the gas chromatographic analysis applied. The new method developed in this work using an internal standard (section 4.5.3) proved to be accurate. This was demonstrated via analyses of prepared feed mixtures for each run. Feed compositions determined via the internal standard method, corresponded to the calculated feed compositions which utilised accurately weighed out masses of feed components (table 4.6). The results obtained via this analysis technique also proved to be repeatable which was demonstrated by undertaking two impurity hydrogenation runs, under the same experimental conditions and similar catalyst loading (runs 1 and 2).

Brown (2005) could not undertake a hydrogen balance due to discrepancies in the mass balances from the results presented in that study. Conversions of impurity and 1-hexene and the yield of n-hexane, suggested that about twice as much hydrogen was consumed than was available in the system according to the chosen H_2/Oil molar ratios and the corresponding settings of the hydrogen mass flow controller. The cause of these discrepancies was attributed by *Brown (2005)* to inaccurate delivery by the hydrogen mass flow controller utilised in the study, which was operating close to its lower limit (5% of scale).

In retrospect, the discrepancies in the mass balance may also be attributed to an inadequate gas chromatographic analysis technique as discussed in the beginning of section 4.5.2. In this study, all hydrogen conversions were below 100%, as

calculated according to equation 16 in section 4.5.4.6 presented in appendix E and table 5.2. This is another indication that the new method is indeed correct.

6.2 Hydrogen dissolution runs

The hydrogen dissolution runs indicated that complete dissolution was achievable under certain operating conditions using the silicon carbide loaded hydrogen dissolver described in section 4.3.3. Furthermore, the results of the hydrogen dissolution runs (section 5.1) established the range of operating conditions under which the hydrogen fed to the hydrogen dissolver achieved complete dissolution in the liquid phase leaving the dissolver and before entering the reactor thus defining a suitable operating window. These results provided a basis for the selective hydrogenation runs.

The figures resulting from the runs (figures 5.1-5.5) show two different types of border lines for possible operating windows, namely a thermodynamic limit, which can be overcome by applying higher operating pressures (see also figure 2.21) and a kinetic limit, which could be overcome by improving the design of the dissolver, most notably by extending its length.

6.3 Stoichiometric and thermodynamic operating limits

The formation of reaction products is governed by the stoichiometric operating limits of the reactions involved (at complete consumption of the available hydrogen) namely:

I. Conversion of 1-hexyne to n-hexane.
II. Conversion of 1-hexene to n-hexane.
III. Conversion of 1-hexyne to 1-hexene.

These relationships are demonstrated in figure 6.1, where limiting cases are utilised to define stoichiometric operating windows. This is done in the figure for a feed of 1 mol% 1-hexyne impurity at differing hydrogen contents. Product composition is dependent on the extent of consumption of hydrogen in the system. It follows that up to 1 mol % hydrogen content the reactions are stoichiometrically limited by the hydrogen content in the system and limited by the impurity concentration at higher hydrogen contents.

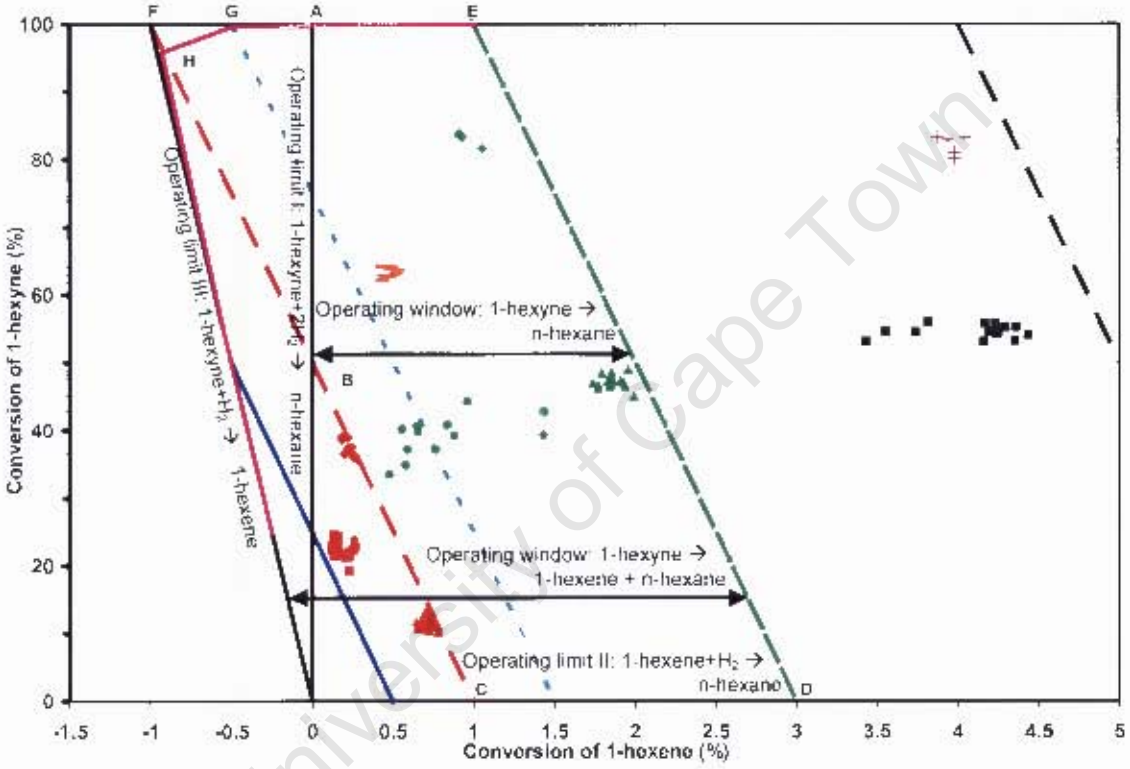

Figure 6.1 Stoichiometric and thermodynamic operating windows defined by hydrogen availability – for 1 mol % 1-hexyne impurity

- Run 1, 30 bar, molar H2/Oil = 0.01
- Run 2, 30 bar, molar H2/Oil = 0.01
- Run 3, 30 bar, molar H2/Oil = 0.03
- Run 4, 10 bar, molar H2/Oil = 0.01
- Run 5, 30 bar, molar H2/Oil = 0.01
- Run 6, 30 bar, molar H2/Oil = 0.03
- Run 6, 60 bar, molar H2/Oil = 0.03
- Run 7, 30 bar, molar H2/Oil = 2 x 0.01[b]
- Run 8, 30 bar, molar H2/Oil = 2 x 0.03[b]
- Run 8, 60 bar, molar H2/Oil = 2 x 0.03[b]

- Limit for 0.5 mol % H_2 content
- Limit for 1.0 mol % H_2 content
- Limit for 1.5 mol % H_2 content
- Limit for 3.0 mol % H_2 content
- Limit for 2 x 3.0 mol % H_2 content
- Thermodynamic equilibrium[a]

[a] For 1.0 mol % 1-hexyne content

[b] Dual dissolver/reactor setup with intermediate hydrogen addition

I. Conversion of 1-hexyne to n-hexane

This simplest case is represented by the y-axis. It corresponds to infinite specificity where 1-hexyne is stoichiometrically converted to n-hexane and no 1-hexene is consumed or formed. The line ends at the upper edge of the graph (point A) where all 1-hexyne is consumed. However, depending on the hydrogen content point A may not be reached. For instance, at a molar H_2/impurity ratio of 1.0, that is 1.0 mol % hydrogen content; conversion of 1-hexyne to n-hexane will be limited to 50 %, corresponding to point B (note that the stoichiometry of the reaction involves 2 moles of hydrogen per mole of 1-hexyne). At molar H_2/impurity ratios ≥ 2.0 point A can be reached but, trivially, the line cannot exceed this point due to the then total consumption of 1-hexyne.

II. Conversion of 1-hexene to n-hexane

This case is represented by the branch of the x-axis that is extending to the right. It corresponds to zero specificity since only 1-hexene loss occurs. The line ends when all hydrogen is consumed. For instance, at a molar H_2/impurity ratio of 1.0, that is 1.0 mol % hydrogen content; conversion of 1-hexene will be limited to 1 %, represented by point C. For 3.0 mol % hydrogen content conversion of 1-hexene will be limited to 3 %, point D.

I + II. Conversion of both 1-hexyne and 1-hexene to n-hexane

This combined case is represented by a triangular shaped window with two of the sides being the Y- and the X-axis. For instance, for a molar H_2/impurity ratio of 1.0 (1.0 mol % hydrogen content) the operating window ranges from the origin to points B and C and is limited by the line between B and C. This line corresponds to complete hydrogen consumption. The area in between points B, C and the origin is the possible operating window under operational conditions. At 3.0 mol % hydrogen content, the limiting line for complete hydrogen consumption ranges from point D to point E and then point A since the line from E to A corresponds to complete consumption of 1-hexyne.

III. Conversion of 1-hexyne to 1-hexene

The 'ideal' case is represented by the 'steep skew' line arising from the origin to point F. 1-Hexyne is stoichiometrically converted to 1-hexene and no n-hexane is formed. The line corresponds formally to negative conversion of 1-hexene and to a specificity of -100. The line ends at the top edge of the graph (point F) when all 1-hexyne is consumed. However, depending on the hydrogen content, point F may not be reached, namely at a hydrogen content < 1.0 mol %.

I + III. Conversion of 1-hexyne to 1-hexene and n-hexane

This case is represented by a triangular operating window with its sides being the Y-axis, the aforementioned 'steep skew' line and the less skew line ranging, less steep, from the Y-axis to the former. For instance, for a hydrogen content of 1.0 mol % the operating window is defined by the lines between the origin and points B and F and the area in between. The line between points B and F marks complete hydrogen consumption. Specificities range from minus infinity (formally) to -100.

I + II + III. Conversion of 1-hexyne to 1-hexene and 1-hexene to n-hexane

The title describes the formal kinetics of the reaction. This case, which combines all aforementioned cases, defines the maximum, or rather, real stoichiometric operating window. For instance, for a hydrogen content of 1.0 mol %, the operating window is defined by the lines between the origin and points C and F with the line from point C to point F representing complete hydrogen consumption. Specificities range (formally) from zero via "± infinity" to -100. For higher hydrogen contents this stoichiometric operating window extends to the right (and only to the right). For instance for a hydrogen content of 3.0 mol %, it is defined by the area origin-D-E-F-origin.

The system, however, is also limited by the approach to thermodynamic equilibrium as discussed in section 5.3. At first, it should be noted that hydrogen consumption is always 'complete', at thermodynamic equilibrium, regardless if the H_2/impurity ratio is stoichiometric or somewhat higher. It can be derived from table 5.3a that up to the highest molar H_2/Oil ratios considered for these calculations, namely 0.03, hydrogen conversion is always > 99.9 %. Table 5.3b and figure 5.23 show that the only product under thermodynamic control would be 1-hexene up to molar H_2/impurity ratios of 1.0 and lower, i.e. with an equimolar and sub-equimolar amount of hydrogen. n-Hexane would be increasingly formed only in case of molar H_2/impurity ratios higher than equimolar (figure 6.1) thus having the 1-hexene consuming the 'excess hydrogen'.

Below a molar H_2/impurity ratio of 1.0, the hydrogenation of 1-hexyne to 1-hexene is thermodynamically strongly favoured, with very little formation of n-hexane. In other words, a net gain of 1-hexene could be obtained under thermodynamic control as long as the H_2/impurity ratio is lower than twice the stoichiometric ratio. Thermodynamic equilibrium limitations affect the limits of the operating windows only marginally and only in regions of very high impurity conversion and specificities close to -100 as indicated in figure 6.1 for the example of 1.0 mol % hydrogen content. Thermodynamics limit the operational window in the top left corner to a line origin-H-G-A.

Data from runs 1 to 8 was fitted to the stoichiometric operating windows to estimate the approach to the limits (data points in figure 6.1). It is obvious that all product mixtures are within the respective hydrogen limitations but far from thermodynamic equilibrium. The product compositions indicate the occurrence of reactions I and II, at least formally, which was also observed by *Brown (2003)*.

Since all results fall to the right of operating limit I, Brown's (2005) conclusion, that 1-hexyne may be saturated straight to n-hexane without forming/desorbing the intermediate 1-hexene, cannot be questioned on this basis.

Thermodynamically, below a molar H_2/impurity ratio of 1.5, 1-hexene would be the preferred product (figure 5.23). However, kinetically, 1-hexyne appears to be preferentially completely saturated to n-hexane (conversion I). Some 1-hexene is consumed, additionally, to also form n-hexane (conversion II). The location of all the data points, somewhere in the middle of the operating window, figure 6.1, may indicate, as outlined above, that conversions I and II are independent with both of them occurring in parallel as long as hydrogen is available.

This is also indicated by comparing the results from runs 1 and 2 with those from run 5 in figures 6.1 and 5.12 and by comparing the results from run 5 and run 7 in figures 6.1 and 5.15 where a decrease in space velocity (runs 1 and 2 to run 5) and an increase in H_2/Oil ratio (run 5 to run 7) lead to an increase in conversions but did not affect specificities.

6.4 Data scatter, repeatability, catalyst stability and reactions without a catalyst

Specificity plots (figures 5.7, 5.9, 5.10, 5.12, 5.15 and 5.18) show that data scatter is small compared to the trends and differences induced by variations of reaction conditions. Figure 5.7, where two runs under identical conditions (with fresh catalyst charge each) are compared, proves repeatability. Throughout the experimental work no inconsistencies in trends occurred. It appeared that catalyst activity slowly declined during runs (figure 5.6). However, the extent of data scatter and the short periods on stream at a certain reaction condition (for only 24 h after the composition of the reactor effluent had stabilised after changing conditions) suggested to refrain from a quantitative determination of this decline.

Nonetheless, given the short run times of typically 120 hours on stream, this loss of catalyst activity was considered negligible. It should be noted that after starting a run the fresh catalyst was allowed to settle in for 24 hours (section 4.4.5).

6.5 Variation of feed impurity concentration

The feed impurity concentration and correspondingly H_2/Oil ratio in run 9 was half that of runs 1 and 2 (table 5.2). The result of this change was similar specificities, whilst conversions of 1-hexyne and 1-hexene were slightly lower (figure 5.9). This is as expected from a bimolecular parallel reaction system where the unsaturated compounds are strongly adsorbed on the catalyst surface, showing reaction orders of (or close to) zero, and the co-reactant (hydrogen) being weakly adsorbed showing a reaction order of 1 (section 2.5.2 and figure 2.14). Obviously, the simultaneous variation of impurity and hydrogen content has only a minor effect. In other words within limits discussed in the following the system is independent of impurity concentration.

6.6 Higher impurity conversions and specificities

The major aim of this work was to achieve higher conversion of impurity than in the study conducted by *Brown (2005),* where a maximum conversion of impurity of approximately 50 % was achieved, at still high or even improved specificities i.e. specificities above 100.

It is obvious from the number of parameters that can be varied in this reaction system, and have been varied, and from the rather complex interaction of these parameters with regard to impurity conversion and specificity, see table 5.2 and specificity plot figures 5.7, 5.9, 5.10, 5.12, 5.15 and 5.18 that the results cannot be discussed and understood parameter-wise. Instead some criteria of higher order must be applied.

6.6.1 Specificity and conversion in the presence of completely dissolved and undissolved hydrogen

In figure 6.2 specificity data is plotted as a function of 1-hexyne conversion for all runs performed.

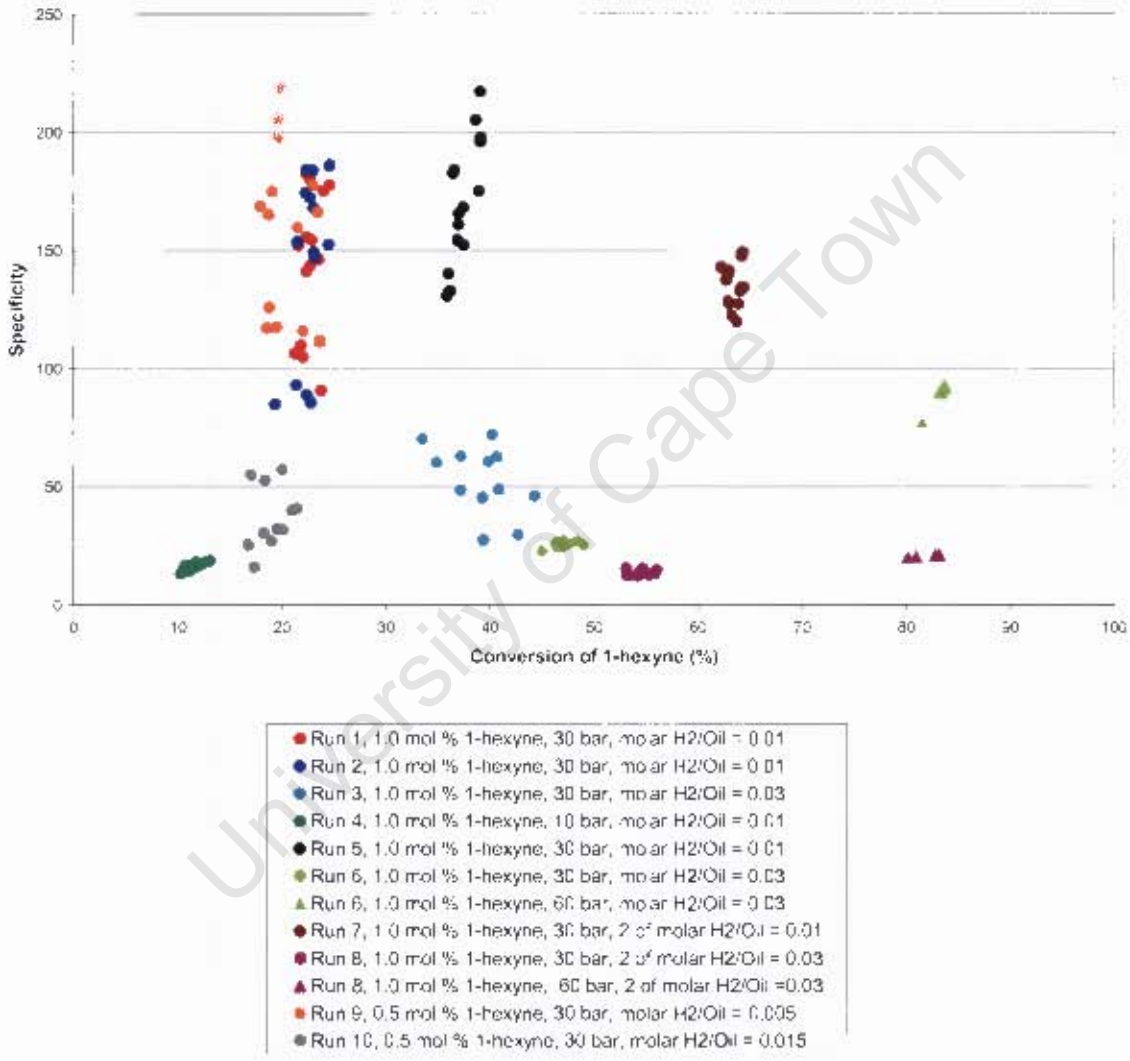

Figure 6.2 Relationship between specificity and 1-hexyne conversion for all runs

At a glance, there are no correlations. However, the relation between specificity and 1-hexyne conversion is clearly determined by the presence or absence of undissolved hydrogen in the reactor. This is illustrated in figure 6.3, where the data points from figure 6.2 are colour coded and thus grouped according to

hydrogen being completely dissolved (**green**), partially undissolved at the reactor inlet but with the unconsumed rest completely dissolved at the reactor outlet (**light orange**) and never completely dissolved (**red**) in the liquid phase according to figures 5.1 to 5.4, section 5.2.1, and table 5.2.

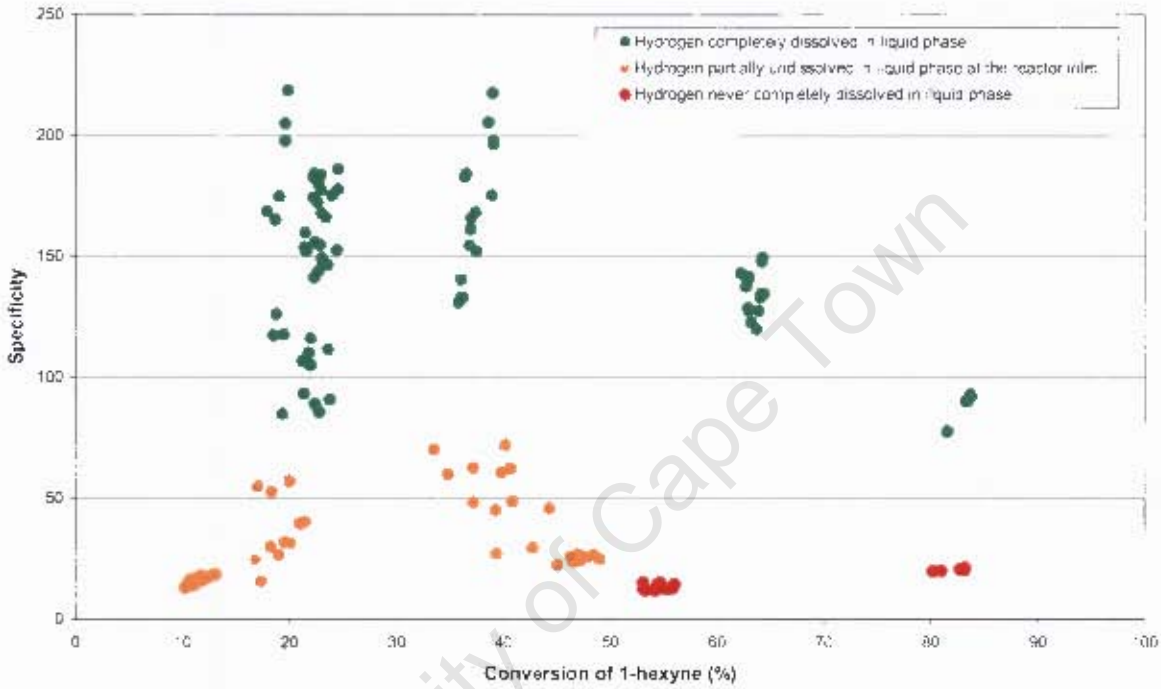

Figure 6.3 Relationship between 1-hexyne conversion and specificity for all runs colour coded according to the presence or absence of undissolved hydrogen

The runs that have been determined as having hydrogen completely dissolved in the liquid phase (**green**) are:

- Runs 1 and 2: The inlet molar H_2/Oil ratio of 0.01 at 30 bar and the low pump rates allow complete dissolution of hydrogen in the liquid phase according to figure 5.2.
- Run 5: The inlet molar H_2/Oil ratio of 0.01 at 30 bar and the low pump rates allow complete dissolution of hydrogen in the liquid phase according to figure 5.2.
- Run 7: The inlet molar H_2/Oil ratio of 0.01 at 30 bar utilised in the first stage and the low pump rate allow complete dissolution of hydrogen in the liquid phase in the first reactor according to figure 5.2. A second hydrogen

stream with the same flow rate was added to the second dissolver. Assuming more than 50% hydrogen consumption in the first reactor (as can be derived from runs 1 and 2, see table 5.2) the total H_2/Oil molar ratio in the second dissolver was < 0.015 and according to figure 5.3 this quantity should have completely dissolved in the oil.

- Run 9: The inlet molar H_2/Oil ratio of 0.005 at 30 bar allows complete dissolution of hydrogen in the liquid phase according to figure 5.1.

The runs that have been determined as likely having undissolved, gaseous hydrogen present at the inlet but not the outlet of the reactor (light orange) are:

- Run 3: The inlet molar H_2/Oil ratio of 0.03 at 30 bar does not allow complete dissolution of hydrogen in the liquid phase according to figure 5.4. However, due to hydrogen consumption along the length of the reactor, all remaining hydrogen may be dissolved at the outlet of the reactor.
- Run 4: The inlet molar H_2/Oil ratio of 0.01 at 10 bar does not allow complete dissolution of hydrogen in the liquid phase according to figure 5.2. However, due to hydrogen consumption along the length of the reactor, all remaining hydrogen may be dissolved at the outlet of the reactor.
- Run 6: The scenario in run 6 is analogous to run 3, just with the addition of a second reactor stage ('large reactor mode'), so that all remaining hydrogen may be dissolved at the outlet of the first reactor, and therefore also dissolved throughout the length of the second reactor.
- Run 10: The inlet molar H_2/Oil of 0.015 at 30 bar is rather close to the thermodynamic limit for complete dissolution, according to figure 5.3, and the fed hydrogen may not have completely dissolved at the reactor inlet. However, due to hydrogen consumption along the length of the reactor, all remaining hydrogen may be dissolved at the outlet of the reactor.

The run that has been determined as almost always having undissolved hydrogen present in the catalyst bed (**red**) is:

- Run 8: The inlet molar H_2/Oil ratio of 0.03 at 30 bar in the first dissolver/reactor stage does not allow complete dissolution of hydrogen in the liquid phase, according to figure 5.4. However, at the lowest space velocities applied, due to hydrogen consumption along the length of the reactor, all remaining hydrogen may be dissolved at the outlet of the first reactor. A second hydrogen stream with the same flow rate was added to the second dissolver. Even when assuming complete hydrogen consumption in the first reactor (as can be derived from run 3, see table 5.2) the total inlet H_2/Oil molar ratio at the second dissolver is at least 0.03 so that the hydrogen would not have completely dissolved in the oil.

The highest specificities were obtained when hydrogen was always completely dissolved. However, a correlation of 1-hexyne conversion with specificity and the presence or absence of gaseous hydrogen is not apparent (figure 6.3).

In figure 6.4 specificity data is plotted as a function of 1-hexene conversion for all runs performed. The figure shows a clear trend, namely, that it is essentially the extent of 1-hexene conversion that determines specificity.

Furthermore, the relation between specificity and 1-hexene conversion is determined by the presence or absence of undissolved hydrogen in the reactor. This is illustrated in figure 6.5, where the data points from figure 6.4 are colour coded and thus grouped according to hydrogen completely dissolved (**green**), partially undissolved at the inlet but with the unconsumed rest completely dissolved at the outlet (**light orange**) and practically never completely dissolved (**red**) in the liquid phase according to figures 5.1 to 5.4, section 5.2.1 and table 5.2.

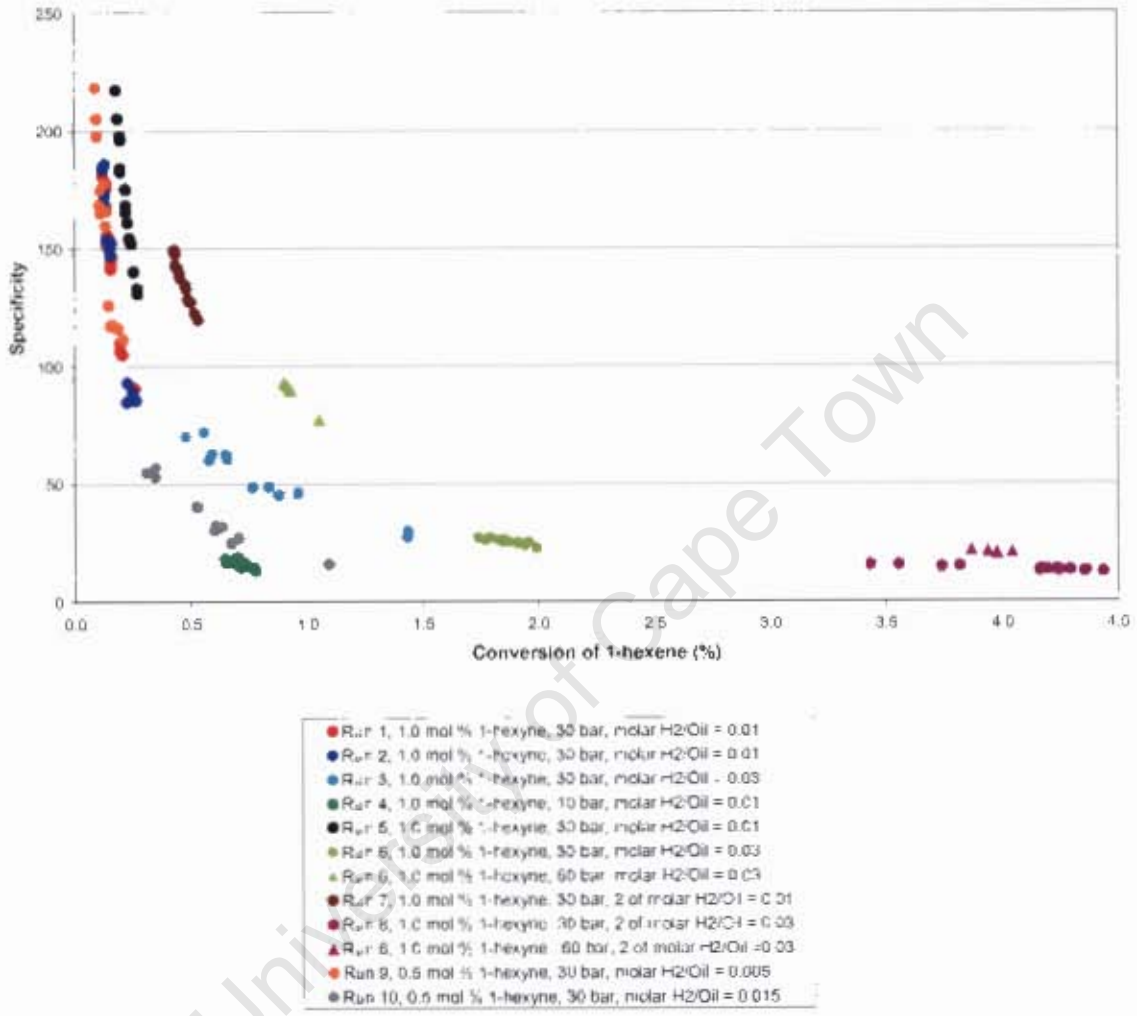

Figure 6.4 Relationship between specificty and 1-hexene conversion for all runs

Apparently, complete dissolution of the hydrogen is one of the crucial parameters (possibly the only one) in selective hydrogenation in the liquid phase. In presence of undissolved hydrogen the conversion of 1-hexene to n-hexane is accelerated which has a detrimental effect on specificity.

6.6.2 Specificity and conversion at stoichiometric and non-stoichiometric hydrogen addition

The results from figures 6.2 and 6.4 may also be grouped and colour coded according to the quantity of hydrogen added to the dissolvers:

- Stoichiometric addition of hydrogen as required for complete conversion (removal) of all highly unsaturated impurity and its conversion to 1-hexene, i.e. molar H_2/impurity ratio = 1 (green)
- Hydrogen addition in excess of the stoichiometric amount (red)

This is illustrated in figures 6.6 and 6.7 where specificity for all runs is plotted against the conversions of 1-hexyne and 1-hexene.

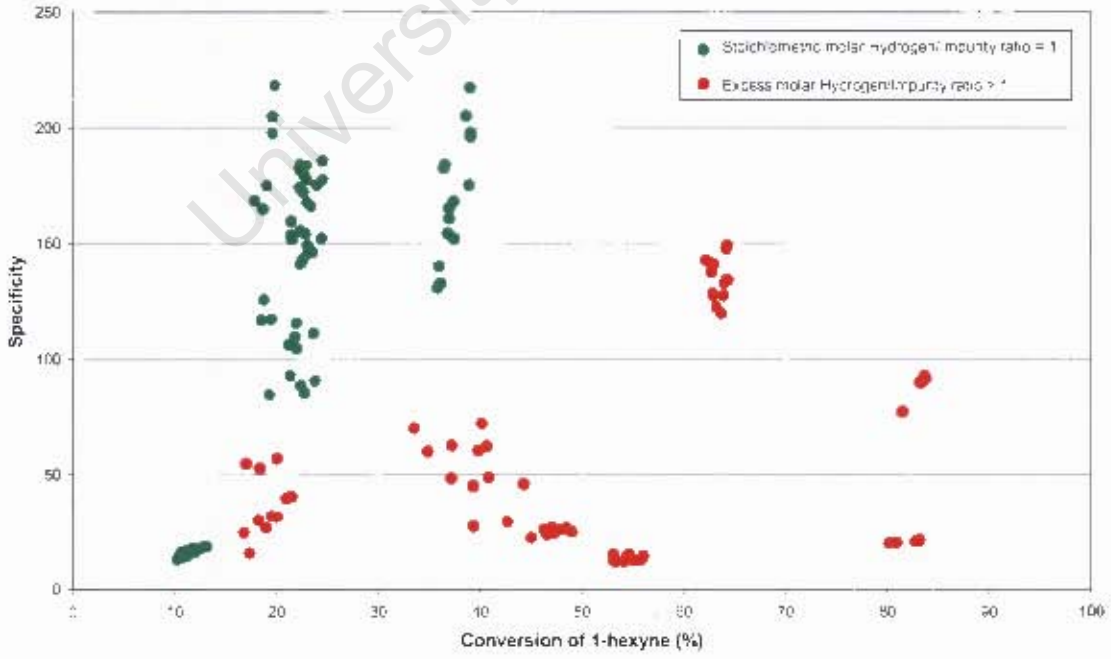

Figure 6.6 Relationship between specificity and 1-hexyne conversion for all runs grouped according to the quantity of hydrogen added to the dissolvers

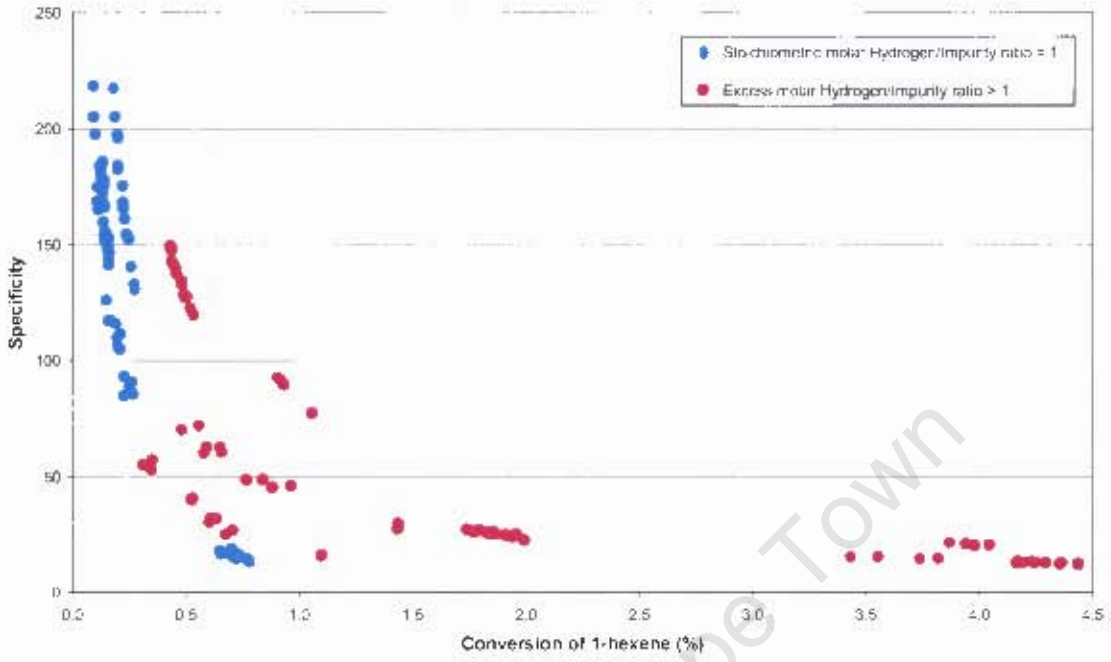

Figure 6.7 Relationship between specificity and 1-hexene conversion for all runs grouped according to the quantity of hydrogen added to the dissolvers

A correlation of specificity with 1-hexyne conversion and stoichiometry is not apparent (figure 6.6). Figure 6.7 seems to show some correlation of specificity with 1-hexene conversion and stoichiometry. However, there are groups of data points of low specificity despite stoichiometric hydrogen/impurity ratio and groups of data points of high specificity despite "excess" hydrogen availability. These data points, obviously, flaw this correlation.

The bottom line is that specificity and molar H_2/impurity ratio show a pseudo-correlation due to the fact that excess hydrogen comes mostly together with undissolved hydrogen and *vice versa*. However, a few exceptions, as discussed above, show this correlation to be only partially complete.

6.7 The effect of linear velocity and space velocity

A reduction of space velocity was achieved by the addition of a second reactor stage (i.e. doubling the catalyst mass) without changing geometry (and hydrodynamics). The comparison of the conversions achieved with one and two reactor stages at the same pump rate, that is twice the residence time but constant linear velocity in the catalyst bed (runs 1 and 2 vs. run 5, figure 5.14), shows that the concentrations of 1-hexyne and hydrogen further decreased, significantly, and that the yield of n-hexane increased whilst the concentration of 1-hexene remained more or less constant. This is as expected when the space velocity is halved.

However, doubling the residence time in single reactor stage mode by halving the pump rate (and, concomitantly, halving the linear velocity in the catalyst bed) did not lead to much of a change in the product composition (figure 5.8 for runs 1 and 2, figure 5.13 for run 5 and figure 5.16 for run 7). Conversions and yields increased only slightly. This result is unexpected and is indicative of external mass transfer limitations controlling the system.

As discussed in section 2.14.3, the decrease in space velocity by decreasing the pump rate increases residence times but also reinforces external mass transfer limitations, should the latter be present. These antagonistic effects lead eventually to the only slight increase in the conversion of 1-hexyne and 1-hexene when halving the space velocity.

Also in section 2.14.3, it is described and illustrated (figure 2.23) that, in the absence of external mass transfer control, conversions must coincide for equivalent space velocities, irrespective of catalyst mass or mass feed rate. In the presence of external mass transfer control, doubling the mass of catalyst would then result in a greater increase in conversion than halving the pump rate, since the latter would also result in a thicker stagnant layer surrounding the

catalyst particles, i.e. a lower mass transfer coefficient, while the former would not. Correspondingly, when running at equal space velocity but different mass of catalyst and the pump rate differing, correspondingly different linear velocity would result and, therefore, different conversion. Conversion would be higher over the longer catalyst bed. This was indeed observed when comparing the results from runs 1 and 2 (single reactor) with the results from run 5 (2 reactors = twice the mass of catalyst) under equal reaction conditions. The difference is obvious. In single reactor stage mode, at WHSV of 7.0 $g_{oil}/g_{cat}.hr$ in runs 1 and 2 (figure 5.8), 1-hexyne conversion was about 20 % and hydrogen conversion was about 60 %, whereas in double reactor stage mode, run 5 (figure 5.13), at the very similar WHSV of 6.1 $g_{oil}/g_{cat}.hr$, 1-hexyne conversion was about 40 % and hydrogen conversion almost complete. This comparison provides strong evidence towards external mass transfer limitations controlling the reaction system when operating at low, typical lab scale linear velocities.

However, these observations are not aligned to *McPherson's (2003),* who observed that hydrogen mass transfer becomes rate limiting at reaction temperatures above 60 °C since *McPherson (2003)* worked at high hydrogen excess (relative to impurity concentration) and in a trickle bed with most of the hydrogen present being in the gas phase. Thus *McPherson (2003)* describes mass transfer control at the gas/liquid interface.

6.8 The effects of varying reaction conditions and catalyst bed configuration on specificity and 1-hexyne conversion

Several of the aspects mentioned in the title of this section have already been dealt with above – or at least in part.

The crucial boundary condition that was found is hydrogen dissolution. Hydrogen dissolution in the liquid reaction mixture must be complete in each and every point of the catalyst bed(s). If this condition is met, specificities in the range of 100-200 are achieved. Any gas phase hydrogen present has a detrimental negative effect on specificity.

6.8.1 The combined effect of space velocity and thermodynamics

It appears that, under conditions of external mass transfer control, the major effect on specificity is via space velocity. It holds throughout that reducing space velocity improves specificity. This improvement comes essentially through a decrease of 1-hexene conversion with decreasing space velocity (figures 5.7, 5.9, 5.10, 5.12, 5.15 and 5.18). This holds, regardless if there is gaseous hydrogen present in the reactor or not.

This result is counter-intuitive but would be in agreement with the observation by *Himelfarb et al. (2002)*, section 2.15 (although unexplained by the authors), that the longer the residence time in the reactor – of an alkene feed with highly unsaturated impurities – the less the hydrogenation of the alkene, while the conversion of the highly unsaturated compound stays high or even increases.

On the other hand it holds in general, provided there is a reaction pathway, that increasing the space time (that is decreasing space velocity) drives a product mixture closer to the thermodynamic equilibrium distribution. Thermodynamic equilibria of 1-hexyne, 1-hexene, n-hexane and hydrogen mixtures have been calculated (section 5.3). It emerges that, thermodynamically, 1-hexene is the favourable product and that practically no n-hexane would be present up to the stoichiometric (i.e. 1:1 molar) H_2/impurity ratio (table 5.3b, figure 5.23 and the top left corner of the operating window in figure 6.1). Up to a molar H_2/impurity ratio of 2 there would still, thermodynamically, be a net production of 1-hexene but then also formation of n-hexane.

Apparently, although this sounds also rather counter-intuitive, the highly unsaturated impurity reacts at first right through to the alkane (section 2.5.1 and figure 2.4 and as derived in section 6.3 based on figures 6.1, 5.12 and 5.15) while a slower, secondary reaction drives this product back to the 1-alkene.

Whatever the case, the subject was not deeply researched in the context of this study and further speculations about the reaction mechanism or specific sites involved will not be drawn.

6.8.2 Hydrogen availability

The other reaction condition that has a major effect is the extent of hydrogen availability and its influence on the rate of impurity and 1-hexene saturation. In the presence of undissolved hydrogen it is mainly the latter reaction that is accelerated. The above shows in table 5.2 and in particular in the following figures:

- Increased H_2/Oil ratio from 0.01 molar (runs 1 and 2) to 0.03 molar (run 3) in the single reactor set up, figure 5.10.
- Increased H_2/Oil ratio from 0.01 molar (run 5) to 0.03 molar (run 6) in the dual reactor set up, figure 5.12.
- Increased H_2/Oil ratio from 2x0.01 molar (run 7) to 2x0.03 molar (run 8, 30 bar) in the dual dissolver/reactor set up with intermediate hydrogen supply and dissolution, figure 5.15.
- Increased H_2/Oil ratio from 1x0.01 molar (run 5) to 2x0.01 molar (run 7) in the dual reactor set up without and with intermediate hydrogen supply and dissolution, figure 5.15.
- Increased H_2/Oil ratio from 1x0.03 molar (run 6, 30 bar) to 2x0.03 molar (run 8, 30 bar) in the dual reactor setup without and with intermediate hydrogen supply and dissolution, figures 5.12 and 5.15.

Increased hydrogen availability accelerates both impurity and 1-hexene conversion simultaneously. However, it should be noted that the specificity drops drastically as soon as the increase in the H_2/Oil ratio results in the presence of undissolved hydrogen (table 5.2) and *vice versa*, in particular when more gaseous hydrogen gets dissolved in the oil phase by increasing the operational pressure.

The effect of increased hydrogen availability shows also in the following:

- Increased pressure from 10 bar (run 4) to 30 bar (runs 1 and 2) in single reactor setup, figure 5.10.
- Increased pressure from 30 bar to 60 bar (run 6) in dual reactor set up, figure 5.12.
- Increased pressure from 30 bar to 60 bar (run 8) in dual reactor set up with intermediate hydrogen supply and dissolution, figure 5.15.

It should be noted that increasing pressure improves specificity (table 5.2) since due to this increase there will be less or no hydrogen in the gas phase.

Finally it appears, although total H_2/Oil ratios deviate to some extent, that interstage hydrogen addition and dissolution (run 7, H_2/Oil ratio molar = 2x0.01) compared to hydrogen addition in one go (run 6, 30 bar, H_2/Oil ratio molar =1x0.03) or working at higher operational pressure (run 6, 30 and 60 bar data points) are measures to avoid the presence of gaseous hydrogen in the catalyst bed and thus improve both specificity and impurity conversion, figures 5.12 and 5.15.

7 CONCLUSIONS & RECOMMENDATIONS

This work extends a series of studies *(McPherson, 2003; Brown, 2005)* on the feasibility of selective hydrogenation for the removal of highly unsaturated impurities, such as hexynes and hexadienes, that may be present in industrial 1-hexene feedstocks intended for use as co-monomers for polyethylene synthesis.

Trivially, the first criterion for the evaluation of the results from such studies is the degree of impurity and impurity isomers removal. *McPherson (2003)* defined the second major criterion, specificity, which is the ratio of the percentages of impurity and impurity isomers removal to the percentage of 1-hexene loss.

The choice of the catalyst, a Pd-Ag/TiO_2 eggshell catalyst (laboratory specimen provided by Süd-Chemie), the choice of the feed mixture, a solution of (as the standard feed mixture) 1-mol % 1-hexyne in 1-hexene, and the choice of the standard reaction conditions of 60 °C reaction temperature, 30 bar reaction pressure, a co-feed of 1 mol % hydrogen and a WHSV range from about 7 g_{oil} / $g_{cat} \cdot h$ to about 12 g_{oil} / $g_{cat} \cdot h$, were also based on this previous experience.

The following progress was achieved compared to *Brown (2005)*:

- The accuracy of the gas chromatographic analyses was improved by developing an internal standard method that allowed accurate quantification of the percentage of the major component in the reaction product, 1-hexene (of around 98 - 99 mol %), the trace percentage of remaining impurity 1-hexyne (between < 0.1 mol % and 1 mol %) and the trace percentage of hydrogenation product n-hexane (between < 0.1 mol% and 1 mol %) in the product samples. It appears that the applicability of this method may be extended to much lower impurity concentrations by adjusting the ratio of the

two weighed in constituents of the standard mixture and injection volumes/split ratios accordingly.

- The new method allowed demonstration of the good balance now achieved between both the conversions of 1-hexene and the highly unsaturated impurity and the yield of the hydrogenation product, n-hexane.
- On this improved basis it was possible to verify the hydrogen balance in the system.
- The functionality of the type of hydrogen dissolver designed and applied by *Brown (2005)* for the purpose of getting all co-fed hydrogen completely dissolved in the liquid feed mixture before reaching the reactor was proven by a specifically designed test device and a specifically developed test method,
- The device allowed a determination of the 'kinetic' limits of the operational window of the dissolver. The kinetic limits determine, in addition to the thermodynamic limits that can be calculated, the pump rate and H_2/oil ratio needed to completely dissolve the hydrogen with a given dissolver.
- The question which was open *(Brown, 2005)* as to whether a stoichiometric H_2/impurity ratio (stoichiometric with regard to impurity conversion to 1-hexene) or the absence of gaseous hydrogen in the catalyst bed is crucial for achieving high specificity, could then be answered in favour of the latter.
- It could be demonstrated that avoidance of the presence of gaseous hydrogen in the catalyst bed is an indispensable requirement and the key to achieving high specificity.
- Indications could be found, however, that limited hydrogen supply, corresponding to the 'stoichiometric ratio', may also be crucial once high impurity conversions are achieved.
- One of the aims of this work was increasing impurity conversion. Impurity conversion could be increased from about 50 %, the maximum percentage achieved by *Brown (2005)*, to 80 - 85 %. Impurity conversion can be

increased by the following means (considering that complete dissolution of the hydrogen must still be achieved):

- Lowering space velocity so that more of the available hydrogen can be consumed (almost complete hydrogen consumption could be achieved by this means).
- Feeding more hydrogen by increasing the H_2/Oil ratio in combination with increasing pressure (so that the hydrogen can still completely dissolve).
- Introducing a second dissolver/reactor stage for intermediate supply of additional hydrogen in order to compensate for the fraction consumed in the first reactor stage.

- Another aim of this work was increasing specificity. Specificity could be increased from about 100, the maximum value achieved by *Brown (2005),* to values around 200.
- Specificity can be increased by operating under conditions that result in very low hydrogen concentrations at the end of the catalyst bed. Accordingly, specificity can be increased by the following means:
  - Limiting the amount of hydrogen fed. The appropriate total amount appears to correspond to the 'stoichiometric ratio' or is only slightly higher.
  - Lowering space velocity so that most of the available hydrogen can be consumed (almost complete hydrogen consumption could be achieved by this means).
  - Increasing the reaction pressure so that the amount of hydrogen required (as, for instance, given by the 'stoichiometric ratio') can be fed at once, not by an additional, intermediate dissolver, so that the initial concentration of dissolved hydrogen in the feed is higher and thus the initial reaction rate and the total hydrogen consumption.

However it was beyond the scope of this study to exploit the aforementioned findings towards maximising impurity conversion and specificity.

It was also found in this study that external mass transfer limitations controlled the system under the conditions applied. This problem must be tackled in future studies.

The phenomenon of external mass transfer limitations controlling the reaction system – not uncommon with laboratory scale tubular reactors – is due to the rather low linear velocities of the fluid phases in the small laboratory scale devices and is even aggravated when comparatively large, technical scale catalyst particles are employed. Since the mass transfer coefficient is not only proportional to the square root of the linear velocity but also to the reciprocal of the square root of the particle diameter *(Fogler, 1999)*, application of a fine diluent in the catalyst bed may help reduce but not eliminate the problem. On a technical scale, due to the much higher linear velocities in these reactors, external mass transfer control of reactions is usually not an issue.

Reducing catalyst particle size drastically can prevent or reduce external mass transfer control. However, this is not applicable to a technical scale eggshell catalyst, such as the catalyst used in this study, without affecting catalyst properties significantly.

In a long and narrow reactor whose internal diameter can, for instance, just accommodate a single catalyst particle, linear velocities would be increased.

However, only part of the external surfaces of the individual catalyst particles packed into such a bed may be exposed to these more rapid streams due to channelling. The problem is illustrated in figures 7.1a to 7.1c for catalyst particles in the form of short cylinders or tablets, such as the catalyst used in this study, and packed into a very narrow reactor tube in different ways.

Indeed, applying a very narrow reactor tube may even worsen the trouble caused by external mass transfer limitations.

However, the problem may be solved applying a structured reactor for laboratory scale studies. In a suitably structured reactor, such as shown in figure 7.1d, the feed is forced to flow over the entire external surfaces of the individual catalyst particles.

Figure 7.1 Catalyst particles in the form of short cylinders or tablets, such as the catalyst used in this study, are packed in different ways into long and narrow reactor tubes whose internal diameters can just accommodate a single catalyst particle. The small squares and diamonds between the individual catalyst particles represent a fine diluent.

a - c: Only part of the external surfaces of the individual catalyst particles packed into these narrow reactor tubes, regardless in which manner, may be exposed to the feed stream due to channelling. The diluent will not be able to force a flow pattern that reaches the entire surface of the catalyst particle (in figure 7.1a, shown as XX in red)

d: The external surfaces of the individual catalyst particles will be completely exposed to the feed stream in a structured reactor.

As mentioned above, a Pd-Ag/TiO_2 eggshell catalyst from Süd-Chemie was applied in this study. This catalyst had all the attributes of a typical selective hydrogenation catalyst but was not designed or optimised by the manufacturer for utilisation in the liquid phase selective hydrogenation of highly unsaturated impurities in a 1-hexene stream. Future investigations may, therefore, also focus on optimising the design of the catalyst.

At last the phenomenon should be addressed that was described by *Himelfarb et al. (2002)* in the context of the selective hydrogenation of alkene streams that contained highly unsaturated impurities. *Himelfarb et al. (2002)* did not offer any explanation or speculation about the possible origin of the observed effect whereby the longer the reaction mixture was exposed to the catalyst, the higher the net gain of alkene was. The key to the understanding of this phenomenon may be the approach of the reaction mixture to thermodynamic equilibrium composition at extended reaction or space times. Provided the highly unsaturated impurity is reacted with an approximately stoichiometric percentage of hydrogen (stoichiometric in terms of the complete conversion of the highly unsaturated impurity to the corresponding alkene) the thermodynamic equilibrium product mixture is almost entirely made up from the alkene with only a small fraction of the impurity remaining and an equally small fraction of the alkane having formed. Possibly this phenomenon can be exploited to achieve high impurity conversions at very high, even negative specificities (that is, when a net production of the 1-alkene is obtained instead of a loss). The major drawbacks could be (i) increased formation of double bond isomers of the 1-alkene and (ii) increased formation of green oils. There are indications in *Himelfarb et al. (2002)* that at least the former was not the case.

8 REFERENCE LIST

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Appendix A - Solubility of hydrogen in 1-hexene

In order to obtain the solubility of hydrogen in 1-hexene for a range of pressures and temperatures, an Aspen Plus simulation was carried out. In this simulation, a stream of hydrogen and a stream of 1-hexene were flashed. The hydrogen was added in a huge excess compared to the amount that could be dissolved in the 1-hexene. The temperature was varied from 0 to 130 °C in intervals of 10 °C and the pressure was set at 1, 15, 25, 30, 40, 60 bar, respectively. The molar percentage of hydrogen in the saturated liquid corresponds to the solubility of hydrogen in 1-hexene at that condition. The maximum temperature at which this is obtainable is limited by the boiling temperature of 1-hexene at the given pressure. The simulation results are given in Table A.1. The results are shown graphically in figure 2.17. It can be presupposed that the addition of 1 mol % 1-hexyne does not change the properties of the solution.

Table A.1 Sensitivity analysis on solubility of hydrogen in liquid 1-hexene, as a function of pressure and temperature (Aspen Plus) with data for the intended reaction temperature (60°C) in bold

Temperature	Solubility of hydrogen in the liquid feed stream (mol %)					
°C	P = 1 bar	P = 15 bar	P = 25 bar	P = 30 bar	P = 40 bar	P = 60 bar
-0.15	0.05	0.78	1.30	1.55	2.05	3.03
9.85	0.05	0.82	1.36	1.63	2.15	3.18
19.85	0.05	0.86	1.42	1.70	2.26	3.34
29.85	0.04	0.90	1.49	1.79	2.37	3.50
39.85	0.04	0.93	1.56	1.87	2.48	3.67
49.85		0.97	1.63	1.96	2.61	3.86
59.85		1.01	1.71	2.05	2.73	4.05
60.00	*a*	**1.01**	**1.71**	**2.05**	**2.73**	**4.06**
69.85		1.04	1.78	2.15	2.87	4.26
79.85		1.07	1.86	2.24	3.00	4.48
89.85		1.09	1.93	2.34	3.15	4.71
99.85		1.11	2.00	2.43	3.29	4.95
109.85		1.11	2.06	2.52	3.44	5.20
119.85		1.09	2.11	2.61	3.59	5.47
129.85		1.05	2.14	2.68	3.73	5.75

a Normal boiling point of 1-hexene is 63 °C.

Appendix B - Calculation of the adiabatic temperature rise in the reactor

Aspen Plus was utilised to simulate the equilibrium between 1-hexyne, 1-hexene n-hexane and hydrogen, in order to calculate the adiabatic temperature rise in the reactor. A reactor model was utilised that calculated simultaneous phase and chemical equilibrium. The reaction scheme modeled is given below. 1-Hexyne is hydrogenated to 1-hexene. 1-Hexene is hydrogenated to n-hexane.

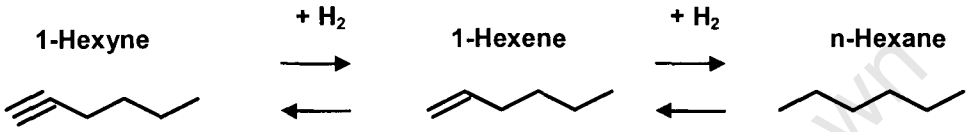


Figure B.1 Reaction scheme modeled in Aspen Plus

The method utilised for calculating the properties of the individual components was the Predictive Redlich-Kwong-Soave equation of state. The feed stream consisted of 1.0 mol% of 1-hexyne in 1-hexene with 1.0 mol% hydrogen addition. This corresponds to an H_2/Oil molar ratio of 1.0 and molar H_2/impurity ratio of 1.0. The reactor inlet temperature was 60 °C and the pressure utilised was 30 bar.

The equilibrium hydrogen conversion under these conditions was > 99%.

The adiabatic temperature rise in the reactor at this condition was 8.7 °C.

Appendix C - Preparation of feed mixture by mass

Molar mass of 1-hexyne = 82.145 g/mol

Molar mass of 1-hexene = 84.161 g/mol

Liquid density of 1-hexene of 0.63 g/ml at 25 °C *(Perrys, 1999)*

1-Hexyne concentration required = α mol %

$$mass\ of\ 1\text{-}hexene\ required = \frac{molar\ mass\ of\ 1\text{-}hexene}{molar\ mass\ of\ 1\text{-}hexyne} \times \left(\frac{100-\alpha}{\alpha}\right) \times mass\ of\ 1\text{-}hexyne\ weighed\ in \quad \text{(B.1)}$$

The actual mass of each of the constituents was measured out accordingly. The actual number of moles of the respective constituent was determined.

$$actual\ number\ of\ moles\ of\ constituent\ added = \frac{actual\ mass\ of\ constituent\ added}{molar\ mass\ of\ constituent} \quad \text{(B.2)}$$

Using the determined numbers of moles of 1-hexyne and 1-hexene their accurate actual mole fractions were calculated.

Suppose a 1-hexyne concentration of 0.5 mol % is required. To make up the necessary feed for a single run of approximately 2 L of solution was, for instance, according to B.1 and B.2:

Mass of 1-hexyne weighed out = 7.0016 g

Therefore, mass of 1-hexene required = 1427.51 g

Assuming density of solution equals density of 1-hexene, the total volume of the solution may be calculated.

$$Volume\ of\ solution = \frac{mass\ of\ 1\text{-}hexene + mass\ of\ 1\text{-}hexyne}{density\ of\ solution} \quad \text{(B.3)}$$

The volume of the aforementioned solution was 2.3 L.

Appendix D - Calibration of mass flow controllers

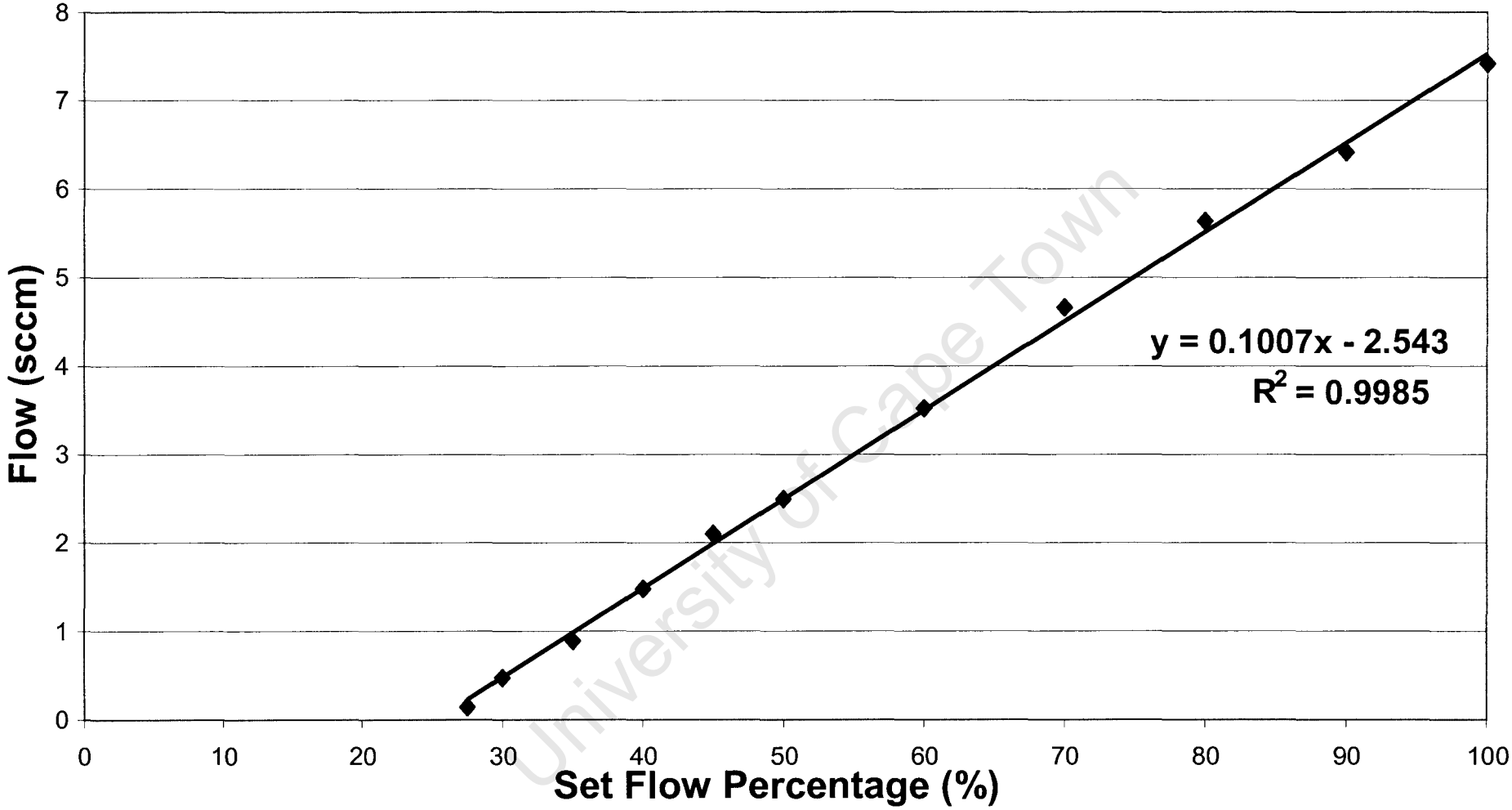
FIC-1 (figure 4.1), the mass flow controller for hydrogen supply to the second dissolver stage was a new state-of-the-art Brooks mass flow controller and the instrument was calibrated using an automatic calibration loop that was installed in the new mass flow controller and the new controller box by making use of the settings within the mass flow controller as follows:

- The display units on the controller box were set to "%". The "%" was set to 100.
- The actual hydrogen flow was measured on the bubble meter and the hydrogen flowrate was calculated in sccm.
- The units on the controller box were set to "sccm".
- The actual hydrogen flowrate from the measurement on the bubble meter (in sccm), at a mass flow controller % setting of 100, was manually entered.
- This procedure was repeated at 0% mass flow controller setting.
- Using these set points and measured values the mass flow controller was calibrated.

In order to check the accuracy of the calibration, an intermediate flow (in %) was set on the display panel of the mass flow controller and compared to the flow measured on the bubble flow meter, converted to sccm. This proved correct and accurate.

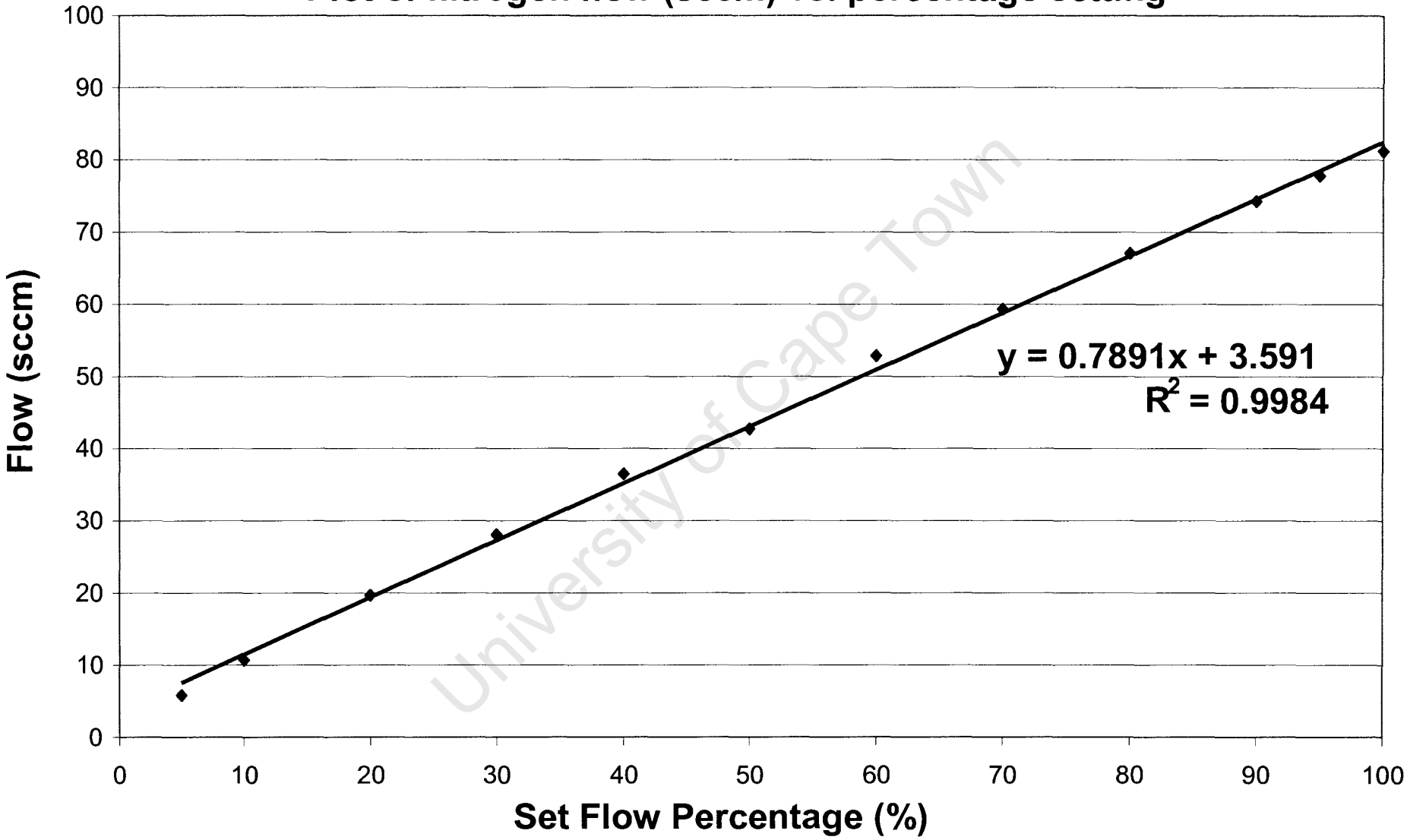
The two "older" mass flow controllers FIC-02 and FIC-03 (figure 4.1) (UNIT mass flow controllers) were calibrated as described in section 4.4.3. Calibration curves are shown in figures C.1 and C.2.

Figure D.1 Calibration graph of mass flow controller FIC-02 (figure 4.1)
Plot of hydrogen flow (sccm) vs. percentage setting



It should be noted that the analog signal from this sensor ramped from 5-20 mA while the controller box was designed for a 0-20 mA signal. This is why the calibration plot cuts the x-axis at about 25 % set flow percentage.

Figure D.2 Calibration graph of mass flow controller FIC-03 (figure 4.1)
Plot of nitrogen flow (sccm) vs. percentage setting



Appendix E - Experimental Data

The mole fractions of the components have been calculated using the method prescribed in section 4.5.4.1 from peak areas obtained from low and high split analysis of each sample (ratio method). The impurity and 1-hexene conversions, specificity and hydrogen conversion were calculated using the equations from section 4.5.4. It is important to note that only net removal of impurity, that is impurity hydrogenation, is considered and thus a conversion of impurity to an impurity isomer is not considered as conversion of impurity. A full analysis of all the components present was not undertaken, as the unidentified peaks form less than 0.5 % of the feed and product samples. Most of these 'unknowns' had been present in the 1-hexene feed and have been found to be inert. The peaks of interest were thus that of the 1-hexyne, 1-hexene and n-hexane which have been considered to be the only components present. The data for each experiment outlined in table 5.2 is shown in the following tables, where both the feed and product data is listed. The internal standard mixture composition is 1.98 mol % 2-methyl pentane and 98.02 mol % cyclohexane. All experiments were undertaken at 60 °C. Peak designations are as in table 4.6.

Experiment 1

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2)

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			1.027	0.224	98.749								
Product	**7.0**	**0.2**	0.775	0.613	98.612	64.092	61.0	0.138	0.131	24.547	23.4	177.66	179
			0.781	0.606	98.613	62.782		0.137		23.972		175.16	
			0.794	0.582	98.624	59.129		0.126		22.709		179.90	
			0.799	0.574	98.628	57.823		0.122		22.265		182.28	
	9.6	**0.275**	0.786	0.625	98.590	64.253	61.3	0.161	0.152	23.530	22.5	146.29	149
			0.793	0.605	98.602	61.539		0.148		22.839		154.47	
			0.795	0.613	98.593	62.169		0.158		22.661		143.47	
			0.798	0.596	98.607	60.175		0.144		22.373		155.57	
			0.806	0.585	98.609	58.250		0.142		21.536		151.96	
			0.798	0.610	98.592	61.491		0.158		22.328		141.25	
	12.2	**0.35**	0.783	0.727	98.490	74.676	67.0	0.262	0.217	23.755	22.2	90.74	103
			0.802	0.657	98.542	65.838		0.209		21.974		104.91	
			0.803	0.644	98.553	64.389		0.198		21.800		109.88	
			0.809	0.639	98.552	63.259		0.199		21.209		106.49	

Experiment 2

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.0699 g Pd-Ag/TiO_2

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			1.016	0.172	98.812								
Product	**7.1**	**0.2**	0.767	0.551	98.682	62.907	59.4	0.132	0.129	24.532	22.9	185.86	178
			0.783	0.528	98.688	58.990		0.125		22.939		183.76	
			0.786	0.532	98.682	59.068		0.132		22.651		172.29	
			0.782	0.541	98.677	60.305		0.137		23.008		167.90	
			0.789	0.518	98.692	57.361		0.121		22.327		184.14	
			0.790	0.524	98.686	57.810		0.128		22.240		174.31	
	9.8	**0.275**	0.768	0.579	98.653	65.551	61.9	0.160	0.153	24.451	23.0	152.40	151
			0.782	0.558	98.659	62.082		0.154		23.038		149.22	
			0.781	0.562	98.657	62.534		0.157		23.123		147.16	
			0.798	0.528	98.674	57.411		0.140		21.455		153.58	
	12.4	**0.35**	0.789	0.648	98.563	70.364	67.7	0.252	0.244	22.370	21.5	88.80	88
			0.785	0.667	98.549	72.623		0.267		22.774		85.55	
			0.799	0.615	98.585	66.042		0.229		21.345		93.09	
			0.820	0.593	98.587	61.715		0.228		19.294		84.87	

Experiment 3

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.03, 1 dissolver, 1 reactor, catalyst mass: 1.090 g Pd-Ag/TiO_2

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			0.944	0.228	98.828								
Product	**8.7**	**0.25**	0.615	1.129	98.255	41.012	43.0	0.579	0.585	34.845	37.7	60.20	65
			0.628	1.017	98.355	36.843		0.478		33.515		70.21	
			0.593	1.164	98.243	42.909		0.592		37.195		62.87	
			0.568	1.253	98.179	46.705		0.656		39.834		60.70	
			0.568	1.253	98.179	47.032		0.651		40.654		62.57	
			0.565	1.158	98.277	43.650		0.557		40.167		72.15	
	11.3	**0.325**	0.593	1.336	98.070	48.641	53.8	0.766	0.862	37.168	40.4	48.54	47
			0.574	1.469	97.957	53.725		0.880		39.262		45.19	
			0.559	1.441	98.000	53.301		0.837		40.840		48.83	
			0.526	1.597	97.877	59.579		0.962		44.286		46.07	
	12.2	**0.35**	0.573	2.018	97.410	72.043	73.1	1.435	1.436	39.352	41.0	27.43	29
			0.541	2.051	97.408	74.204		1.436		42.704		29.73	

X

Experiment 4

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 10 bar, molar H_2/Oil = 0.01, 1 dissolver, 1 reactor, catalyst mass: 1.1075 g Pd-Ag/TiO_2

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			1.034	0.225	98.741								
Product	**6.9**	**0.2**	0.898	1.056	98.046	96.685	96.6	0.705	0.719	13.112	12.4	18.70	17
			0.901	1.044	98.055	95.237		0.695		12.856		18.59	
			0.906	1.050	98.045	95.294		0.706		12.393		17.58	
			0.919	1.102	97.979	99.241		0.772		11.131		14.43	
	9.4	**0.275**	0.910	1.072	98.017	97.131	95.7	0.733	0.741	11.951	10.9	16.31	15
			0.921	1.096	97.983	98.508		0.768		10.960		14.35	
			0.928	1.101	97.971	98.262		0.780		10.260		13.16	
			0.926	1.044	98.030	92.701		0.721		10.423		14.48	
			0.922	1.032	98.046	92.015		0.704		10.871		15.50	
	12.0	**0.35**	0.915	1.026	98.059	92.006	90.6	0.691	0.679	11.507	11.4	16.70	17
			0.913	0.986	98.102	88.254		0.648		11.747		18.17	
			0.912	1.016	98.072	91.392		0.678		11.816		17.44	
			0.923	0.980	98.097	86.605		0.653		10.713		16.50	
			0.916	1.075	98.008	96.807		0.742		11.370		15.32	
			0.919	0.996	98.085	88.668		0.664		11.160		16.87	

Experiment 5

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01, 1 dissolver, 2 reactors, catalyst mass: 1.0748 g Pd-Ag/TiO_2 in first reactor, 1.1093 g Pd-Ag/TiO_2 in second reactor

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			0.995	0.200	98.805								
Product	**3.5**	**0.2**	0.607	0.766	98.627	95.436	95.0	0.180	0.194	39.038	38.1	217.46	197
			0.606	0.786	98.608	97.466		0.199		39.081		196.19	
			0.606	0.785	98.609	97.365		0.198		39.104		197.77	
			0.611	0.771	98.619	95.498		0.188		38.637		205.26	
			0.631	0.760	98.608	92.416		0.199		36.571		184.09	
			0.633	0.760	98.608	92.187		0.199		36.419		182.66	
	4.8	**0.275**	0.608	0.807	98.585	99.361	97.3	0.222	0.231	38.905	37.4	175.31	163
			0.623	0.792	98.585	96.471		0.223		37.423		168.20	
			0.622	0.816	98.561	98.909		0.246		37.470		152.18	
			0.627	0.796	98.577	96.342		0.230		36.977		160.99	
			0.627	0.789	98.584	95.714		0.224		36.990		165.48	
			0.628	0.803	98.569	96.933		0.239		36.851		154.39	
	6.1	**0.35**	0.637	0.812	98.551	97.065	98.3	0.257	0.269	36.015	36.0	140.21	134
			0.639	0.827	98.534	98.344		0.274		35.814		130.76	
			0.635	0.830	98.535	99.006		0.273		36.202		132.86	
			0.636	0.827	98.536	98.590		0.272		36.052		132.93	

Experiment 6

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 and 60 bar, molar H_2/Oil = 0.03, 1 dissolver, 2 reactors, catalyst mass: 1.1186 g Pd-Ag/TiO_2 in first reactor, 1.1039 g Pd-Ag/TiO_2 in second reactor

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			1.050	0.195	98.755								
30 bar													
Product	**4.3**	**0.25**	0.561	2.437	97.002	91.065	91.9	1.775	1.791	46.613	47.0	26.26	26
			0.564	2.425	97.011	90.526		1.766		46.274		26.21	
			0.556	2.407	97.037	90.201		1.740		47.038		27.09	
			0.542	2.476	96.982	92.988		1.795		48.439		27.01	
			0.555	2.497	96.948	93.261		1.830		47.175		25.79	
			0.562	2.500	96.938	93.116		1.839		46.514		25.29	
	5.6	**0.325**	0.577	2.636	96.787	97.128	95.7	1.993	1.912	45.041	46.7	22.61	24
			0.559	2.510	96.930	93.543		1.847		46.747		25.31	
			0.550	2.527	96.924	94.420		1.854		47.677		25.72	
			0.562	2.600	96.838	96.469		1.941		46.529		23.99	
			0.553	2.578	96.869	95.996		1.910		47.316		24.78	
			0.555	2.591	96.854	96.352		1.924		47.135		24.50	
	6.0	**0.35**	0.540	2.536	96.924	95.036	95.5	1.853	1.879	48.594	48.1	26.25	26
			0.551	2.509	96.940	93.750		1.838		47.494		25.86	
			0.554	2.536	96.910	94.558		1.868		47.221		25.30	
			0.535	2.644	96.821	98.791		1.958		49.029		25.04	
60 bar													
Product	**4.3**	**0.25**	0.176	1.985	97.839	88.814	89.3	0.927	0.943	83.239	83.2	90.12	91
			0.171	1.966	97.863	88.321		0.903		83.690		92.83	
			0.194	2.093	97.713	91.818		1.055		81.541		77.35	
			0.174	1.989	97.837	89.010		0.929		83.438		90.08	
			0.175	1.989	97.835	88.974		0.931		83.309		89.80	
			0.170	1.979	97.851	88.789		0.915		83.782		91.80	

Experiment 7

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.01 to each of the dissolvers, 2 dissolver / reactor stages, half of the H_2 added to each of the dissolvers, catalyst mass: 1.0889 g Pd-Ag/TiO_2 in first reactor, 1.0741 g Pd-Ag/TiO_2 in second reactor

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			1.007	0.232	98.761								
Product	**3.5**	**0.2**	0.360	1.305	98.335	86.033	86.0	0.431	0.447	64.274	63.4	149.22	142
			0.373	1.307	98.320	85.453		0.446		62.956		141.29	
			0.361	1.350	98.289	88.233		0.478		64.165		134.34	
			0.380	1.289	98.330	84.209		0.436		62.231		142.84	
			0.376	1.314	98.310	85.706		0.457		62.710		137.43	
			0.361	1.307	98.332	86.090		0.434		64.181		147.79	
	4.8	**0.275**	0.359	1.354	98.287	88.519	87.6	0.480	0.477	64.372	63.6	134.30	134
			0.374	1.312	98.314	85.639		0.452		62.854		139.61	
			0.362	1.353	98.285	88.306		0.482		64.029		132.91	
			0.373	1.355	98.271	87.881		0.496		62.954		127.42	
	6.2	**0.35**	0.370	1.380	98.249	89.260	89.1	0.518	0.511	63.224	63.4	122.54	125
			0.363	1.372	98.265	89.178		0.502		63.911		127.45	
			0.365	1.399	98.235	90.448		0.532		63.710		119.79	
			0.374	1.349	98.277	87.519		0.490		62.883		128.49	

Experiment 8

1.0 mol % 1-hexyne in 1-hexene, 60 °C, 30 and 60 bar, molar H_2/Oil = 0.03 to each of the dissolvers, 2 dissolver / reactor stages, half of the H_2 added to each of the dissolvers, catalyst mass: 1.0889 g Pd-Ag/TiO_2 in first reactor, 1.0741 g Pd-Ag/TiO_2 in second reactor)

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			1.013	0.225	98.762								
30 bar													
Product	**3.5**	**0.2**	0.461	4.470	95.069	79.925	86.2	3.739	4.103	54.447	55.4	14.56	14
			0.445	4.564	94.991	81.761		3.818		56.035		14.68	
			0.447	4.973	94.580	88.541		4.234		55.839		13.19	
			0.447	4.908	94.645	87.458		4.169		55.811		13.39	
			0.452	5.026	94.522	89.337		4.293		55.312		12.89	
			0.452	5.094	94.454	90.472		4.362		55.313		12.68	
	4.8	**0.275**	0.459	4.289	95.252	76.951	82.0	3.554	3.869	54.644	54.1	15.37	14
			0.475	4.154	95.371	74.431		3.434		53.074		15.46	
			0.461	4.972	94.567	88.302		4.248		54.457		12.82	
			0.463	4.962	94.575	88.096		4.240		54.230		12.79	
	6.2	**0.35**	0.464	5.156	94.381	91.312	88.7	4.436	4.287	54.180	53.8	12.21	13
			0.473	5.065	94.462	89.657		4.354		53.288		12.24	
			0.475	4.873	94.652	86.429		4.162		53.110		12.76	
			0.460	4.921	94.618	87.464		4.196		54.528		13.00	
60 bar													
Product	**3.5**	**0.2**	0.170	4.887	94.942	91.739	92.9	3.868	3.961	83.189	82.0	21.52	21
			0.175	4.954	94.872	92.772		3.939		82.755		21.01	
			0.171	5.061	94.768	94.627		4.044		83.145		20.56	
			0.201	4.967	94.832	92.559		3.979		80.172		20.15	
			0.193	4.973	94.834	92.792		3.977		80.960		20.36	

Experiment 9

0.5 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.005, 1 dissolver, 1 reactor, catalyst mass: 1.090 g Pd-Ag/TiO_2

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}.hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			0.471	0.128	99.401								
Product	**7.0**	**0.2**	0.379	0.319	99.302	56.704	55.9	0.099	0.094	19.619	19.7	197.68	210
			0.379	0.315	99.306	55.909		0.096		19.589		205.12	
			0.378	0.312	99.310	55.490		0.091		19.856		218.51	
			0.378	0.312	99.310	55.490		0.091		19.856		218.51	
	8.7	**0.25**	0.361	0.378	99.261	72.089	63.0	0.141	0.122	23.396	20.6	166.16	169
			0.363	0.365	99.272	68.980		0.129		22.958		177.53	
			0.370	0.363	99.267	67.245		0.135		21.464		159.61	
			0.383	0.329	99.288	57.775		0.113		18.694		164.96	
			0.387	0.318	99.295	54.819		0.106		17.890		168.54	
			0.381	0.326	99.292	57.525		0.109		19.038		174.86	
	12.2	**0.35**	0.368	0.420	99.212	79.024	73.3	0.189	0.175	21.957	20.5	115.99	118
			0.360	0.450	99.190	86.583		0.212		23.601		111.45	
			0.379	0.385	99.236	69.649		0.166		19.473		117.49	
			0.383	0.365	99.252	64.981		0.149		18.758		125.89	
			0.384	0.372	99.244	66.273		0.158		18.500		117.12	

Experiment 10

0.5 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, molar H_2/Oil = 0.015, 1 dissolver, 1 reactor, catalyst mass: 1.091 g Pd-Ag/TiO_2

	WHSV	Pump rate	Mole fractions			Conversion (%)						Specificity	Average specificity
	(g_{oil}/g_{cat}-hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)	H_2	Average H_2	1-Hexene	Average 1-hexene	1-Hexyne	Average 1-hexyne		
Feed			0.518	0.112	99.370								
Product	**8.7**	**0.25**	0.414	0.564	99.022	37.046	35.0	0.351	0.336	20.020	18.4	57.11	55
			0.430	0.508	99.062	32.292		0.310		17.018		54.92	
			0.423	0.553	99.024	35.748		0.348		18.346		52.82	
	12.2	**0.35**	0.407	0.749	98.844	49.892	51.7	0.529	0.565	21.478	20.7	40.58	37
			0.409	0.743	98.848	49.280		0.525		20.960		39.89	
			0.407	0.746	98.847	49.593		0.526		21.325		40.51	
			0.414	0.846	98.740	55.852		0.634		20.085		31.69	
			0.417	0.819	98.764	53.867		0.610		19.520		32.02	
	13.9	**0.4**	0.423	0.806	98.771	52.529	63.3	0.603	0.770	18.243	17.8	30.28	27
			0.419	0.912	98.668	59.896		0.706		18.985		26.88	
			0.428	1.290	98.282	84.545		1.095		17.345		15.83	
			0.431	0.870	98.699	56.305		0.675		16.782		24.86	

Experiment 11

0.5 mol % 1-hexyne in 1-hexene, 60 °C, 30 bar, no hydrogen addition, 1 dissolver, 1 reactor, catalyst mass : 1.090 g Pd-Ag/TiO_2

	WHSV	Pump rate	Mole fractions		
	(g_{oil}/g_{cat}-hr)	(ml/min)	1-Hexyne (A_1)	n-Hexane (A_2)	1-Hexene (A_4)
Feed			0.527	0.101	99.373
Product	**8.7**	**0.25**	0.522	0.125	99.353
	12.2	**0.35**	0.513	0.107	99.380
	13.9	**0.4**	0.527	0.097	99.376